

EVALUATION OF CORROSIVENESS, OXIDATION, AND WEAR PROPERTIES OF HYDRAULIC AND RECOIL FLUIDS

INTERIM REPORT

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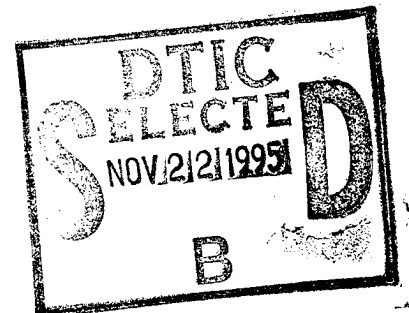
By

**P.I. Lacey, D.W. Naegeli, and B.R. Wright
U.S. Army TARDEC Fuels and Lubricants Research Facility (SwRI)
Southwest Research Institute
San Antonio, Texas**

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| 13. ABSTRACT (Maximum 200 words) This document outlines a laboratory study to define the interrelated parameters of degradation and wear of contacts lubricated with various hydraulic fluids, with particular reference to chlorotrifluoroethylene (CTFE). The results rank the likely wear, corrosiveness, and oxidation properties of CTFE in comparison to currently used silicone-, polyalphaolefin-, and mineral oil-based fluids. Particular attention was given to the metallurgy of critical components specific to the gun recoil brake mechanism. In general, the antiwear characteristics of the CTFE fluid were found to be similar to those of petroleum but marginally inferior to polyalphaolefin-based oils. However, CTFE produced severe corrosion of each of the major components in brass at temperatures above approximately 135°C. As a result, operation at very high temperatures is likely to cause unacceptable material removal from copper-based metallurgies. The report also details the results of tests performed to define the lubricating characteristics of a low viscosity polyalphaolefin-based single hydraulic fluid, intended to allow operation in low temperatures. The results indicate good boundary lubricating characteristics with the expected reduction in hydrodynamic lift. | | | | |
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EXECUTIVE SUMMARY

Problems and Objectives: Hydrocarbon-based hydraulic fluids qualified under MIL-H-6083 are highly flammable. A fire resistant, polyalphaolefin (PAO)-based fluid, qualified under MIL-H-46170, was developed in the 1970s, and more recently, a nonflammable chlorotrifluoroethylene (CTFE) fluid produced. However, the PAO fluid has significantly increased viscosity at low temperature, while the CTFE fluid is not compatible with the existing hydraulic system. The objectives of the present study are to evaluate the corrosion and wear characteristics of both fluids with particular regard to a gun recoil application.

Importance of Project: Hydraulic systems are a central part of many military vehicles and represent a significant fire hazard due to their high operating pressures and applications throughout the vehicle. The present study defines the tribological characteristics of alternative fluids with significantly reduced flammability. The data should be useful during component design, particularly for the CTFE fluid, which is not compatible with current hydraulic systems. In addition, surface treatment processes were identified to minimize potential side effects, evident under more severe operating conditions with CTFE.

Technical Approach: Laboratory-scale tests were performed to evaluate the corrosion and wear resistance of both CTFE- and low viscosity PAO-based hydraulic fluids. For the purposes of comparison, baseline tests were also performed using mineral oil, silicone, and a PAO-based oil qualified under MIL-H-46170. The test parameters were directed towards conditions and metallurgy expected to exist within the gun recoil brake system. The test surfaces were analyzed using Auger Electron Spectroscopy (AES) and Electron Spectroscopy for Chemical Analysis (ESCA) to define the material removal mechanisms present.

Accomplishments: At normal operating temperatures, the level of wear observed with both the low viscosity PAO- and the CTFE-based oils is comparable to that with conventional hydrocarbon fluids qualified under MIL-H-6083. However, use of CTFE under high temperature operating conditions (above 135°C) may result in corrosion of copper and bronze materials. Conventional PAO oil qualified under MIL-H-46170 had the best boundary lubricating characteristics of the oils evaluated, as opposed to the silicone-based fluids, which provided the worst wear resistance.

Military Impact: The results of the present study demonstrate that both the CTFE and low viscosity PAO fluids have excellent antiwear and corrosion properties that are at least equal to fluids qualified under MIL-H-6083. However, the CTFE fluid is significantly different to conventional oils, particularly with respect to high temperature stability and degradation mechanisms. The permissible range of operating temperatures are defined depending on metallurgy, and a number of surface treatment processes are identified to minimize corrosion under more severe conditions.

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I. OBJECTIVE

The primary objective of this study is to define the potential effects of new and degraded chlorotrifluoroethylene (CTFE)-based nonflammable hydraulic (NFH) fluid on wear, with particular reference to a gun recoil brake mechanism. Conventional mineral oil-, silicone-, and polyalphaolefin (PAO)-based hydraulic fluids are used as a baseline for comparison. A secondary objective is to evaluate the lubricating characteristics of a low viscosity, single hydraulic fluid (SHF).

II. INTRODUCTION

MIL-H-6083 (1)*, a petroleum-based hydraulic fluid, has been used as the recoil fluid in artillery and as the hydraulic fluid in most Army ground equipment since World War II. Military aircraft used the equivalent MIL-H-5606 (2) fluid. The petroleum-based fluid performs well in the recoil brake system, except that it is flammable.(3) In the 1970s, PAO-based fluid qualified under MIL-H-46170 (4) [MIL-H-83282 for aircraft (5)] was developed as a replacement for MIL-H-6083, since it is less flammable and has slightly better wear characteristics. The PAO fluid has been widely used in military vehicles, but remains a fire threat under certain conditions. Work was initiated in 1975 at the Air Force Materials Laboratory of Wright Patterson Air Force Base to develop a thermally stable, nonflammable hydraulic fluid.(6) A range of fluids was considered, including phosphate esters, silicones, cyclic esters, and fluorinated phosphonates. CTFE was ultimately selected, primarily due to its excellent fire resistance, although cost, availability, useable temperature range, viscosity-temperature properties, thermal stability, additive solubility, density, and compressibility were also considered.

CTFE is compatible neither with the existing fluids qualified under MIL-H-46170 and MIL-H-6083 nor with current hydraulic systems. A number of problems were initially associated with the practical use of CTFE, although appropriate additives appears to produce an acceptable fluid.

* Underscored numbers in parentheses refer to the list of references at the end of this report.

However, the complex interactions of the fluid's physical and chemical properties, combined with the severe thermal and mechanical stresses imposed during boundary lubrication, are largely undefined. As a result, application-specific wear testing of CTFE-based hydraulic fluids is required.

Currently, the U.S. Army is considering NFH fluid for use in the gun recoil brake for the next generation, self-propelled howitzer. Full-scale system components may be used to define the relative wear resistance of an additive package or metallurgical pair. However, such testing is more easily performed using bench-scale wear tests. As a result, the most critical components and contact areas within the gun recoil brake assembly were identified, and a bench wear test methodology was developed, cognizant of the conditions expected to exist in practical operation. Nonflammable and silicone fluids were compared to baseline fluids that have a known performance in full-scale equipment.

III. BACKGROUND

A considerable amount of research has already been performed with CTFE and a number of problems resolved. The CTFE-based fluids initially failed to meet a number of target property requirements, including bulk modulus, wear rate, and viscosity index (VI).⁽⁷⁾ The relative change in viscosity with increasing temperature was initially controlled using a VI improver. However, VI improvers were not included in later fluids, as viscosity loss at high shear rate was experienced with the VI-improved CTFE. In addition, the properties of the baseline fluid alone were found to be sufficient, after the requirements for VI were relaxed. Nonetheless, many contacts in the hydraulic system are partially separated by a hydrodynamic film, and the viscosity and pressure-viscosity coefficient of the NFH fluid are appreciably less than for equivalent hydrocarbon-based (petroleum and PAO) fluids, as shown in Fig. 1.⁽⁸⁾ The net result is likely to be increased intermetallic contact between components that are in relative motion.

ASTM STANDARD VISCOSITY-TEMPERATURE CHARTS
FOR LIQUID PETROLEUM PRODUCTS (D 341)
CHART III: KINEMATIC VISCOSITY, HIGH RANGE, DEGREES CELSIUS

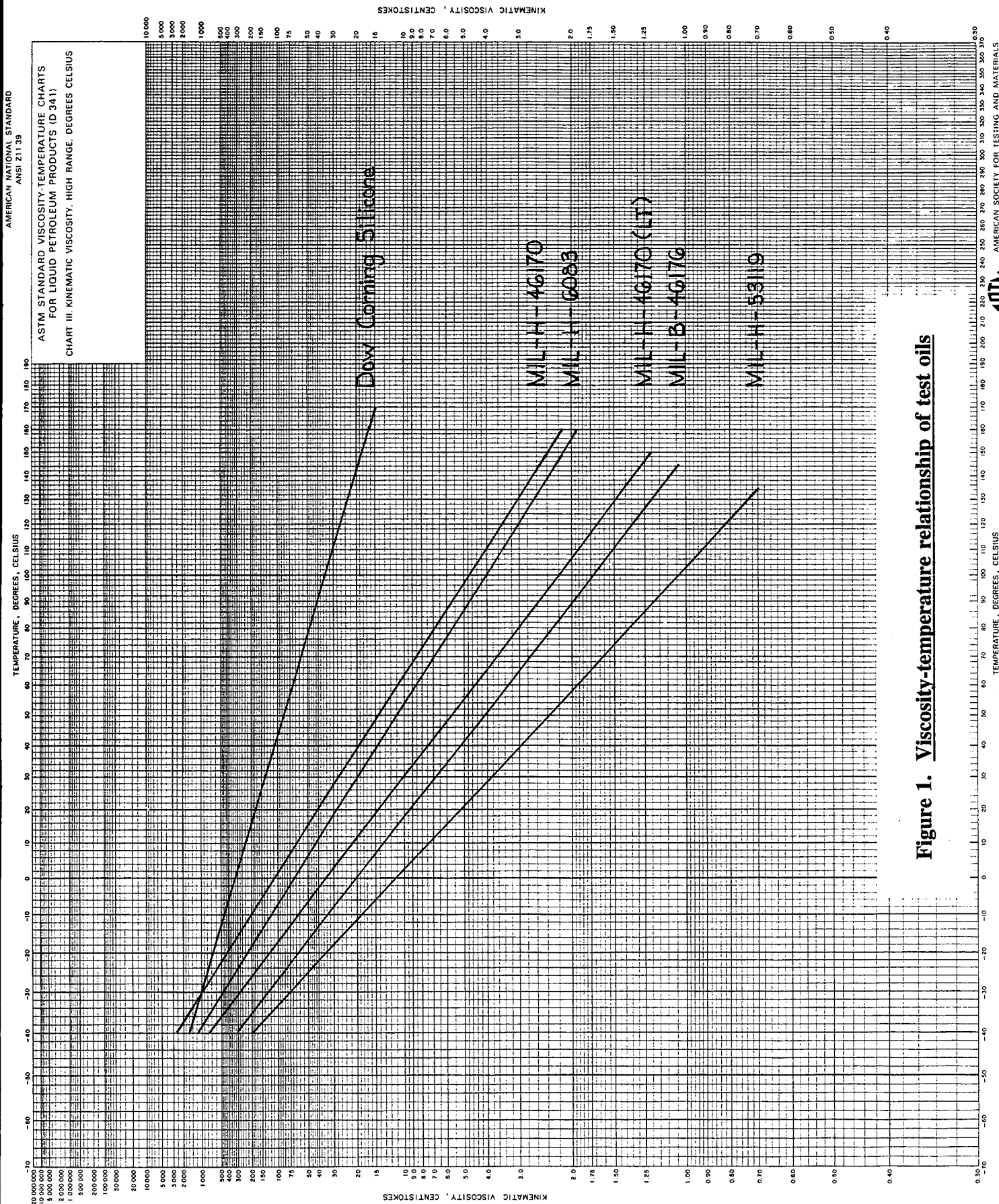


Figure 1. Viscosity-temperature relationship of test oils



If the contact conditions are sufficiently severe, thick film lubrication fails and intermetallic contact is prevented by a thin boundary film. The original CTFE basestock produced relatively severe wear when tested under boundary conditions and failed to meet the traditionally required 1.0-mm wear scar diameter produced in the four-ball wear test.(7) Many additives commonly used in hydrocarbon-based oils, such as tricresyl phosphate, are not effective in CTFE (7) due to a number of factors, including poor additive solubility. However, several additives, including molybdenum dialkyldithiophosphate, have produced a dramatic reduction in the wear rate observed with the base fluid. The formulated CTFE fluid used in the present work contains a fluorinated sulfonamide and a zinc dinonylnaphthalene sulfonate as antiwear and antirust agents, respectively.

The primary function of the gun recoil brake is to dissipate the reaction force generated by the artillery round as heat. The temperature generated within the brake system depends on a range of factors, including ambient temperature, firing frequency, and the number of firing cycles. The maximum temperature of the bulk fluid has yet to be defined but is expected to approach 165°C.(9) However, very localized areas of intersparsity contact may reach temperatures considerably in excess of this value, due to frictional heating. The MIL-H-53119 (10) specification requires that the fluid be suitable for use in the temperature range -54°C to 135°C. Previous work with CTFE basestock has shown that the fluids degrade at temperatures above 232°C (6), although the presence of copper, iron, and tin accelerated the degradation process and produced measurable degradation at 175°C for 72 hours. Discoloration and possible corrosion of other materials, such as bronze, has also been observed in full-scale pump loop tests.(7) An operating temperature of 175°C also corresponds to the Advanced Field Artillery System (AFAS) operating envelope.

The importance of this surface reaction on the overall wear mechanism with CTFE fluids has not been defined. However, work with other slightly corrosive fluids has indicated that the combined effects of mechanical wear and chemical corrosion can result in total material losses that are much greater than the effects of each process alone.(11) Chemically corroded surface layers are commonly softer than the metallic substrate and are easily removed. Under appropriate conditions, such as with an extreme pressure agent, the formation of a softer layer will prevent

adhesive welding and seizure. More commonly, however, excessively strong surface chemical reaction may increase wear rate by either a pure corrosive wear mechanism or corrosion-induced fatigue. As a result, this higher temperature--which corresponds to the AFAS operating envelope--was requested by the sponsor and was selected for the maximum test temperature in the present study.

IV. APPROACH

The primary objective of this study is to define both wear resistance and high-temperature stability of MIL-H-53119 hydraulic fluid and to evaluate the remaining oils (TABLE 1) as a baseline for comparison. Two fluids formulated from PAO basestocks were evaluated: one was a MIL-H-46170 qualified product, and the other was a candidate single hydraulic fluid (intended for use in very cold operating conditions) that does not yet have a military specification. All but two of the oils are qualified under military standards, as detailed in TABLE 1. The second oil without a standard (100 cSt Dow Corning silicone) is composed of polydimethyl-siloxane fluid, with a more complete description provided in Appendix E. The NFH fluid qualified under MIL-H-53119 is composed of approximately 99 percent CTFE basestock complemented by small amounts of corrosion inhibitor and antiwear additives. The formula for the CTFE fluid is $\text{Cl}(\text{CF}_2\text{CFCL})_n\text{Cl}$, with n normally equal to 3. Some higher molecular weight oligomers are also present. The precise composition of the CTFE fluid used in this work (as defined using gas chromatography in Appendix F) is unknown but is not identical to that used in Reference 6. These differences are likely to be due to batch variations in the concentrations of oligomers in the fluid. Each of the unused fluids was evaluated for both high-temperature stability and wear resistance. A more detailed description of the test methodology follows.

TABLE 1. Principal Characteristics of Test Fluids

| Specification No. | Base Fluid | Fire Resistance | Viscosity, 100°C, cSt | Specific Gravity | Pour Point, °C | Bulk Modulus, kPa, min. |
|-------------------|---------------|-----------------|--------------------------|---------------------|-------------------|----------------------------|
| MIL-H-6083 | Petroleum | Flammable | 5.2 | 0.86 | -59 | 1.45×10^6 |
| MIL-H-53119 | CTFE | Nonflammable | 1.0 | 1.7 | -60 | 1.24×10^6 |
| MIL-H-46170 | PAO | Fire Resistant | 3.6 | 0.85 | -54 | 1.38×10^6 |
| None* | Low Visc. PAO | Fire Resistant | 2.6 | 0.844 | -63 | |
| MIL-B-46176 | Silicone | Fire Resistant | 12.6 | | | |
| None | Silicone | Fire Resistant | 31.0 | 0.964 | -65 | |

* Referred to as single hydraulic fluid (SHF)

A. Test Methodology for Evaluation of Oil Stability

High temperatures are generated within many modern highly loaded hydraulic systems. MIL-H-5606, MIL-H-6083, MIL-H-46170, and MIL-B-46176 (12) each require a minimum corrosiveness and oxidation stability according to the procedure outlined in References 13 and 14. In each instance, test coupons of a specific copper and/or brass composition are specified, along with other metallurgies such as steel and aluminum.

In the present study, the effects of oil degradation in a real environment are simulated using a modified version of ASTM D 4636 (15), which is an amalgamation of References 13 and 14. A wide range of temperatures was used to define the useful operating range of the fluid. Test coupons of C-93200 high lead tin bronze, copper alloy NR 955, and 4140 steel were immersed in the oil bath to act as catalysts and to evaluate the fluid corrosivity. These nonstandard coupons were manufactured from different sections of the recoil brake assembly. Metallurgies which may be prone to corrosion by the MIL-H-53119 fluid were given particular attention, and a number of surface treatment processes were evaluated. Finally, oxidation-corrosion tests were performed with coupons manufactured from pure copper, lead, zinc, and tin, which are the primary elements present in the C-93200 material.

The oxidation-corrosion tests were performed with each of the five formulated oils detailed in TABLE 1 at 135 and 175°C to reflect the predicted normal and absolute maximum operating temperatures of the gun recoil mechanism, respectively. Oxidation-corrosion tests were also performed at 135°C using the available **basestock** fluids for the purpose of comparison. During testing, dry air was continuously bubbled through each fluid at a rate of 10 L/hr to facilitate the oxidation process, with reflux condensers at the outlet from each reservoir to minimize the effects of oil evaporation. Previous studies have shown that degradation of hydrocarbon fluids is accelerated by the presence of water; however, little moisture is likely to be available within the confines of the gun recoil brake system. Oil samples were periodically removed from the test reservoir, and degradation was defined from measurements of viscosity, total acid number (TAN), and mass loss from the metallic coupons. This process indicates the interrelated effects of both metallurgy on lubricant degradation and acidic oil reaction products on the corrosion of specific metals. In addition, selected samples were examined using Fourier Transform Infrared (FTIR) spectroscopy and gas chromatography (GC) in an attempt to highlight any change in the molecular structure of the oil.

Limited testing of CTFE was also performed in a nitrogen atmosphere. These tests were performed at 135 and 175°C and define the potential corrosivity of CTFE in the absence of oxygen, such as in a closed hydraulic system. It is believed that oxygen affects the corrosion rate of metals in CTFE through a metal-catalyzed auto-oxidation reaction. Test coupons of C-93200 were immersed in the fluid during both tests, as these were the only metallurgies found to be corroded by CTFE in an oxygen atmosphere.

In instances where appreciable corrosion was present on the metallic test coupons, surface analysis was performed using Electron Spectroscopy for Chemical Analysis (ESCA) or X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES). ESCA or XPS and AES are related surface analysis techniques that can provide elemental concentration and oxidation state (or chemical bonding) information on elements located on surfaces and below (down to about 100 angstroms or 10 nanometers). XPS can obtain information on both nonconductive and conductive surfaces, while Auger electron (photoelectron) spectroscopy can provide an image of surface topographical features of conductive surfaces and can obtain

elemental concentration information in "surface atomic percent." XPS also provides "surface atomic percent" information. In the case of this study, it appears that somewhat greater sensitivity was obtained in the XPS analysis work than in the Auger work. XPS, which uses an X-ray beam to excite the surface atoms (thus generating photoelectrons), is a more gentle technique than Auger analysis, which uses electron beam bombardment (resulting in the generation of Auger photoelectrons).

Both XPS and AES techniques involve high vacuums; hence, only solid samples (metals, polymers, ceramics, or liquids at very low temperatures) can be analyzed. In the work done on the C-93200 bronze (high-leaded tin type) specimen, XPS and AES provide information on the exposed (i.e., not covered with hydraulic fluid) metal surfaces and on nonvolatile CTFE hydraulic fluid (strongly adsorbed, partially oxidized or degraded, or of sufficient molecular weight as to not be volatile).

B. Test Methodology for Wear Resistance

Contact loading, geometry, temperature, atmosphere, oil history, surface topography, and the relative compatibility of the opposing metallurgical pairs play a critical role in defining the overall wear rate. A wide range of potentially viable test methodologies exists for the evaluation of wear resistance. MIL-H-5606 and MIL-H-6083 each specify a maximum wear scar diameter of 1.0 mm for petroleum-based hydraulic fluids using the four-ball wear test, performed according to ASTM D 2266¹. Similarly, MIL-H-53119, which applies specifically to CTFE, requires a four-ball wear test result of less than 0.8 mm in diameter². Many previous studies have examined the wear resistance of hydraulic fluid using the four-ball technique (8, 16), although the unidirectional sliding of a highly loaded, counterformal AISI E-52100 steel contact may not reflect the conditions present in the recoil brake mechanism. Nonetheless, four-ball wear tests were performed on each of the fluids in this study according to ASTM D 4172. No attempt was made to define the ultimate load carrying capacity of the fluid, as it is likely that the

¹ A revised procedure specifically for use with lubricating fluids (ASTM D 4172) is now available.

² MIL-H-53119 also requires a 500-hour hydraulic pump loop test.

conformal contacts within the gun recoil mechanism will be lightly loaded. In addition, previous workers have found that ultimate load carrying capacity has little relationship with the wear observed in most operating hydraulic systems, as practical contacts are typically operated under conditions more moderate than those required for seizure.(17)

The Cameron-Plint Wear Test Apparatus, shown in Fig. 2, is intended primarily for the rapid assessment of the performance of lubricants and lubricant metal combinations. In this test, an upper specimen slides on a lower plate with a pure sinusoidal motion, driven by a variable speed motor. The lower (fixed) specimen is mounted in a stainless steel oil bath attached to a heater block. The opposing (oscillating) specimen is loaded using a spring balance, with an applied load of between 0 and 250 Newtons (N). The resulting friction force may then be measured using a piezoelectric force transducer. The standard apparatus allows test temperature to be adjusted from ambient to 450°C. For this study, the apparatus was modified to allow low-temperature testing to better reflect the typical operating conditions for the low viscosity single hydraulic fluid. During these tests, a modified base for the fluid reservoir was chilled using recirculated ethylene glycol provided by a small refrigeration unit. This configuration allowed testing at temperatures as low as -8°C. Initial testing in an open environment produced excessive

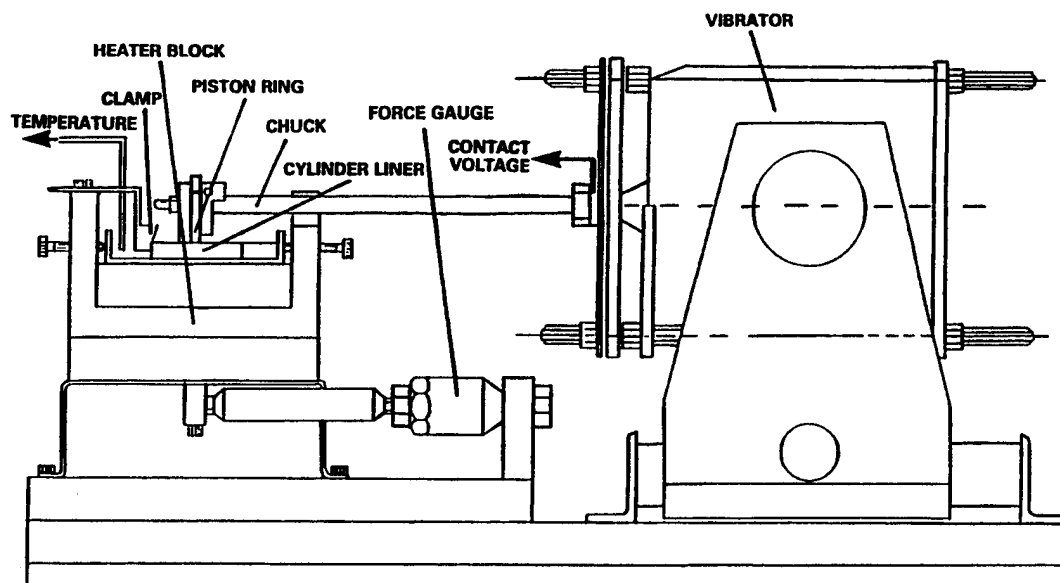


Figure 2. Schematic diagram of the Cameron-Plint wear test apparatus

moisture condensation and ice around the fluid reservoir. An enclosure was placed around the test cell and filled with dry air to minimize moisture availability. Subsequent tests indicated that condensation was greatly reduced but not eliminated.

The contact conditions likely to exist during operation of the full-scale gun recoil brake mechanism have not been precisely defined. Indeed, it would appear likely that a very wide range of contact loads may exist, depending on the transient forces generated during firing, degree of misalignment, and the location of the piston within its range of travel. As a result, the present study attempted to compare fluid performance over the range of conditions available on the Cameron-Plint. The peak sliding speed available in the reciprocating contact of the laboratory test apparatus is approximately 700 mm/s, with an average of 500 mm/s. This value is appreciably less than the peak sliding speed produced in the gun recoil brake mechanism. However, most severe metallic contact and resulting wear will normally occur at the beginning and end of the piston travel, as a relatively thick hydrodynamic film is likely to be present at higher speeds. During the present work, wear tests performed as a function of sliding speed were carried out over a constant sliding **distance**, instead of the more usual constant sliding **duration**. This methodology ensures that tests carried out over a range of sliding speeds are directly comparable (simply dividing by the effective sliding distance takes no account of the low-contact pressures formed beneath highly worn specimens nor the effects of running-in).

Previous workers have found that successful evaluation of hydraulic fluids in laboratory wear tests requires use of metallurgy similar to that found in the final component.⁽¹⁷⁾ As a result, three different contact configurations and metallurgies were used from different sections of the gun recoil brake mechanism. For ease of reference, a code number was assigned to each contact pair, as detailed in TABLE 2. The specimens for contacts A, B, and C were machined from components within the gun recoil brake mechanism. (Selected metallurgical properties from each contact pair are defined in TABLE 3.) This procedure ensures that the metallurgy, hardness, and surface finish of the full-scale component are faithfully duplicated. After completion of wear tests with contact types A, B, and C, any variation in surface topography and the depth of the wear scar produced was measured using a Talysurf surface profilometer.

TABLE 2. Summary of Contact Configurations and Metallurgies

Contact A

| | |
|----------------|---|
| Components: | Piston head/sleeve |
| Metallurgy: | 4340 steel per AMS 6414/copper alloy NR 955 (ASTM B271) |
| Configuration: | Conformal |
| Surfaces: | As in component specification |

Contact B

| | |
|----------------|---|
| Components: | Rod/end cap head |
| Metallurgy: | Chrome-plated 4340 steel/weld overlay on 4340 steel |
| Configuration: | Conformal |
| Surfaces: | As in component specification |

Contact C

| | |
|----------------|---|
| Components: | Sleeve bearing/cylinder body |
| Metallurgy: | C-93200 high-leaded tin bronze/4140 steel |
| Configuration: | Conformal |
| Surfaces: | As in component specification |

Contact D

| | |
|----------------|--|
| Components: | Manufactured spns. (similar to sleeve bearing/cylinder body) |
| Metallurgy: | C-93200 high-leaded tin bronze/4140 steel |
| Configuration: | Counterformal |
| Surfaces: | Polished to mirror finish/4.16-mm radius |

Contact E

| | |
|----------------|---|
| Components: | Surface-modified manufactured specimens |
| Metallurgy: | Surface-treated C-93200 bronze flat 0.5-in. diameter AISI E 52100 steel ball |
| Configuration: | Counterformal |

TABLE 3. Physical Characteristics of Wear Test Metals and Surface Finish as Machined From Gun Recoil Components

| Metallurgy | Density, kg/m ³ | Hardness (Hv), kg/mm ² | RMS Roughness, μm* |
|----------------------|-------------------------------|--------------------------------------|-----------------------|
| C-93200 | 8,150 | 90 | 2.01 |
| 4140 Steel | 7,800 | 360 | 0.39 |
| 4340 Steel | 7,800 | 380 | -- |
| Chrome-plated 4340** | -- | 380 | 0.74 |
| Weld overlay on 4340 | -- | 130 | 0.72 |
| NR955 | 8,900 | 225 | 1.57 |
| AISI E 52100 | 7,810 | 680 | 0.034 |

* = The Root Mean Square (RMS) surface roughness applies to contacts A, B, and C, as defined in TABLE 2. The surface roughness of the polished surfaces in contact D are defined in the body of the text.

** = The true surface hardness of the chrome-plated 4340 steel may be considerably in excess of the substrate value.

The metallurgy in contact configuration D is similar to that of contact C and was selected due to the susceptibility of C-93200 bronze to corrosion by CTFE fluid, as indicated by the oxidation-corrosion tests detailed in Section V-A of this report. The purpose of configuration D is to provide more rapid screening and comparative tests over a wide range of contact conditions, with the most critical metallurgy in both new and used oils. A schematic diagram of configuration D is shown in Fig. 3. The upper C-93200 bronze specimen consists of a spherical end machined on commercially available rod stock, with a surface finish of approximately 0.3 μm. The opposing 4140 steel test flat is highly polished using 1-μm diamond paste to a Root Mean Square (RMS) surface roughness of 0.04 μm to minimize abrasion and adhesion and emphasize the effects of corrosive wear. Use of the counterformal contact with highly polished surfaces also facilitates accurate wear measurement by optical microscopy after a relatively short test duration. The total wear volume, V , may then be derived from the mean wear scar diameter, D , using the relationship defined in Equation 1.

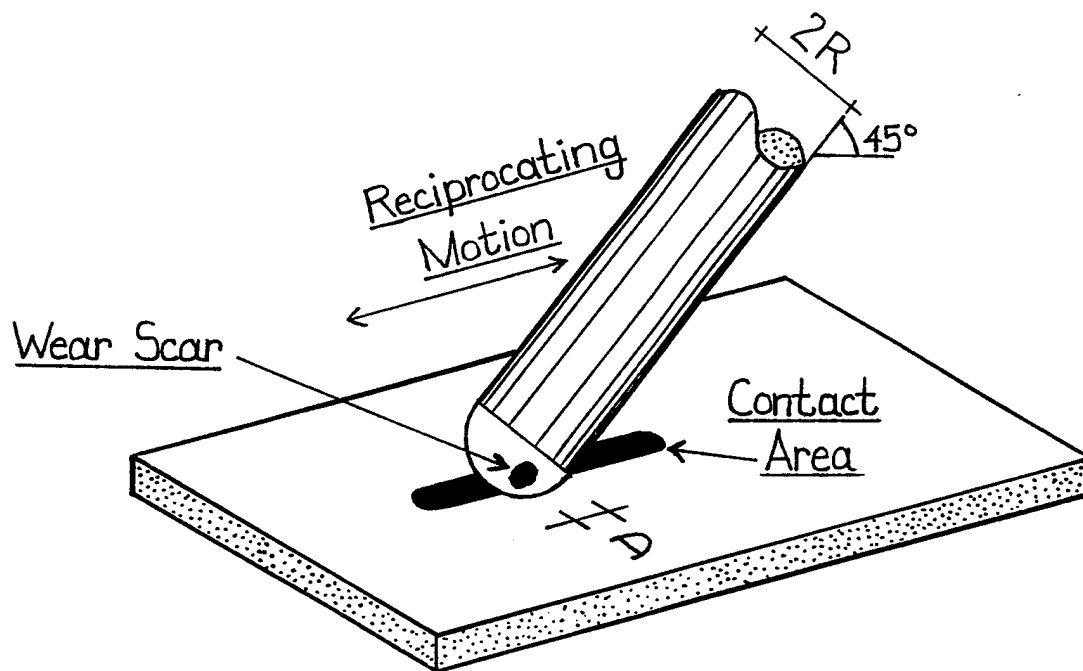


Figure 3. Schematic diagram of the pin on flat geometry (configuration D in TABLE 2)

$$V = \frac{(\pi \times D^4)}{(64 \times R)} \quad (\text{Eq. 1})$$

where R = ball diameter (4.16 mm).

Contact E was designed to allow wear testing of various surface treatment processes intended for use with C-93200 bronze. Once again, a counterformal contact geometry was selected to allow accurate wear measurement. However, in contrast to contact D, the C-93200 material (which is the treated specimen) was machined to form the test flat, rather than the reciprocating ball contact. Previous experience has shown that the surface coating would be almost immediately removed if applied to the Hertzian contact on the test ball. However, treatment of the test flat introduces a much larger surface-treated area, with only intermittent contact due to the motion of the test ball. The wear volume was measured from the test flat using a Talysurf surface profilometer. No wear measurement was taken on the much harder opposing AISI E 52100 steel ball.

Prior to tabulation, the calculated wear volume was normalized using the fundamental equation discussed by J.F. Archard.^(18, 19) The technique was originally applied to adhesive wear; however, it also provides a convenient and widely accepted nondimensional measure of wear for many rubbing systems. The law may be expressed for a contact with a wear volume V (mm^3), on a surface of hardness H_v (kg/mm_2), and applied load L (kg), over a sliding distance d (mm), as follows:

$$K = \frac{VH_v}{3Ld} \quad (\text{Eq. 2})$$

Although Archard's law was derived based on continuous unidirectional sliding contact conditions, research conducted by Stowers and Rabinowicz ⁽²⁰⁾ shows it can be applied equally well for predicting the wear of metals under the condition of alternating sliding contact, as used in the present study.

The effects of elastic deformation on the unworn counterformal specimens was calculated using Hertzian equations, as detailed in Reference 21, with the results given in Fig. 4. The corresponding apparent wear volume and Archard's wear coefficient are also plotted to allow comparison with the results given in subsequent sections³. In general, the apparent material loss due to elastic deformation is appreciably less than the true wear volume. The decreased contact pressure present beneath the worn specimens will further reduce the effects of elasticity, making it negligible in practice.

³ Archard's coefficient was calculated for a wear volume corresponding to the elastic contact width at a sliding distance of 85.6 m, used in most tests with the counterformal contact.

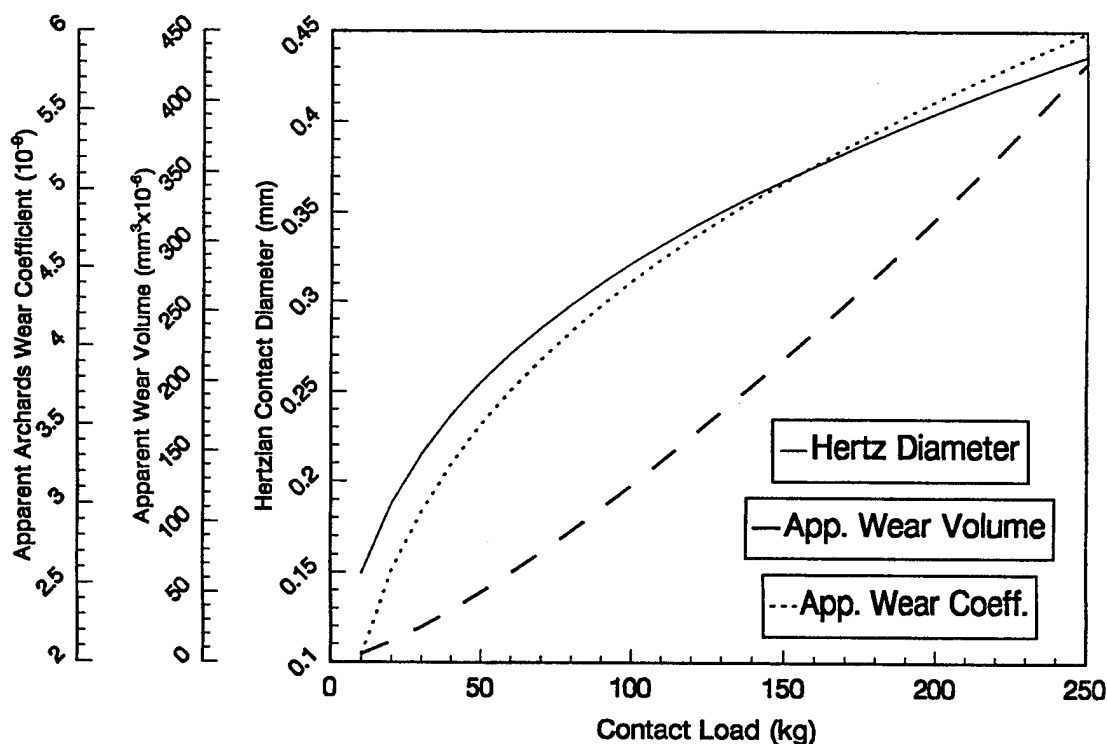


Figure 4. Calculated Hertzian contact diameter, corresponding apparent wear volume, and Archard's wear coefficient due to elastic deformation of Contact D

V. RESULTS

A. Oxidation-Corrosion Tests

1. Oxidation-Corrosion Tests at 135°C

Oil degradation as reflected by TAN and kinematic viscosity during oxidation-corrosion tests at 135°C are shown in Appendix A for the base fluid that does not contain additive. As expected, rapid degradation of the uninhibited PAO and petroleum basestock was observed, with no initiation period (Fig. A-1⁴). The naturally occurring oxidation inhibitors are incapable of preventing degradation at this temperature (the synthetic PAO fluid is likely to have no natural inhibitors). By comparison, the unformulated CTFE fluid appeared to remain completely stable, with no change in either acid number or viscosity. The high acid number for the unformulated

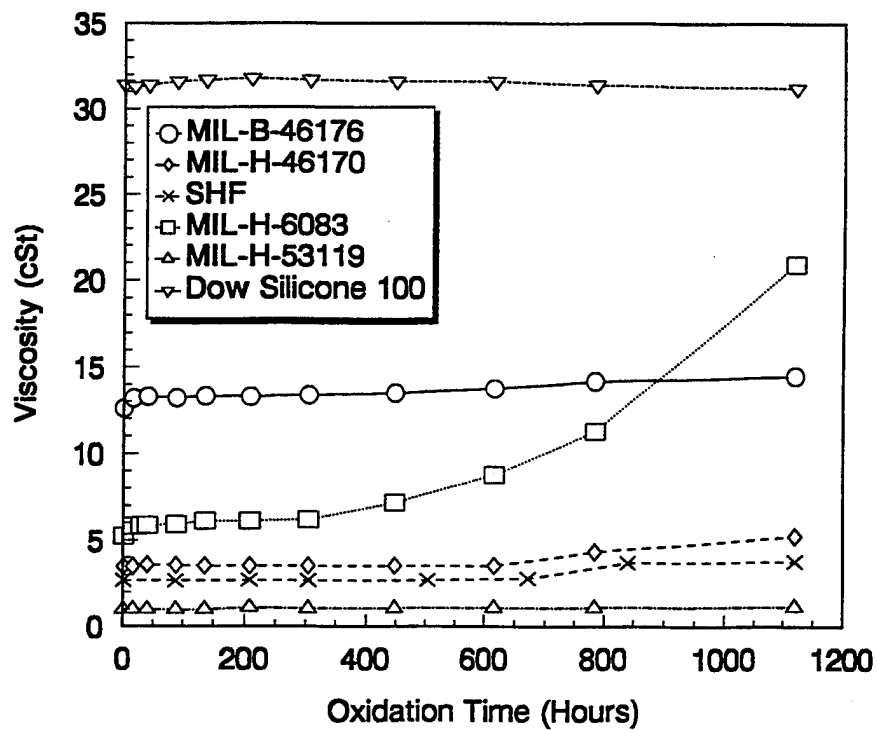
⁴ The more important summarizing figures are contained in the body of the text. The remaining figure numbers have a character prefix which denotes the appropriate appendix.

PAO- and petroleum-based fluids caused slight mass loss from the C-93200 bronze specimen (the results of tests with a measurable mass loss may be found in Fig. A-2). Some mass loss was also observed for the unformulated CTFE fluid with the bronze metallurgy. No measurable corrosion was present on 4140 steel with any of the unformulated oils.

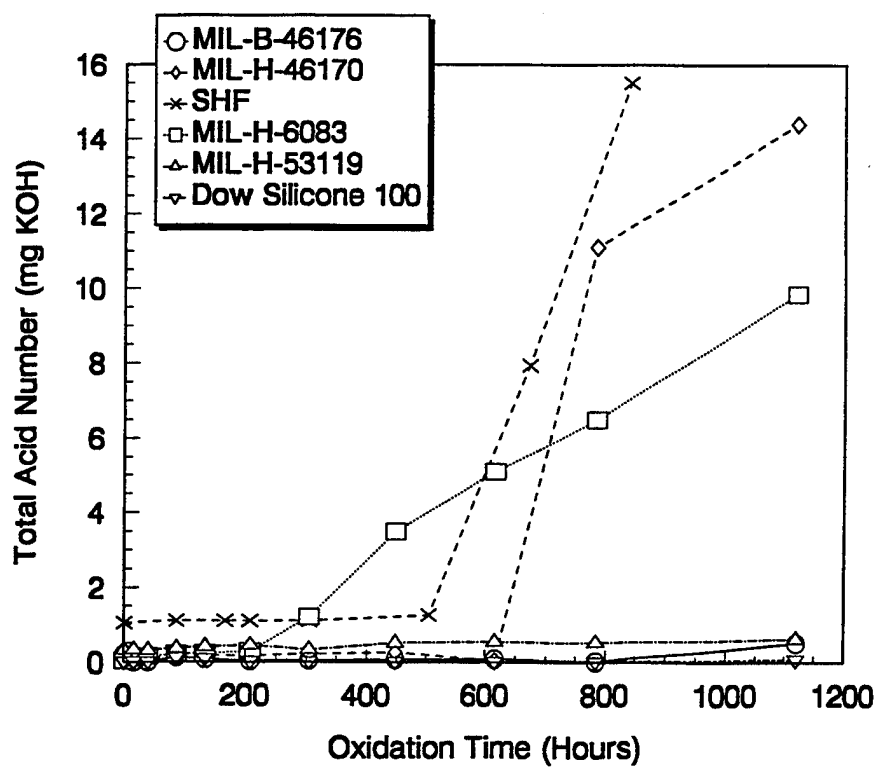
Oil degradation, as reflected by TAN and viscosity, for fully formulated fluids that contain additive are shown in Fig. 5. As expected, the stability of the formulated hydrocarbon oils at 135°C is greatly improved in comparison to their basestocks. The characteristics of the CTFE and the highly stable silicone fluids remain unchanged throughout the duration of the 1,100-hour oxidation-corrosion test, while the petroleum- and PAO-based fluids break after an induction period of 300 and 600 hours, respectively. The lower viscosity PAO-based single hydraulic fluid failed slightly before the higher viscosity PAO oil. The dramatic break for each of the fluids is probably due to exhaustion of the oxidation inhibitor additives, thereby allowing rapid degradation similar to that produced by the base oil. This break is most evident from measurement of TAN, while no change occurred in the viscosity of the PAO fluid. No metallic corrosion was observed with either the hydrocarbon- or silicone-based oils, despite the high acid number achieved in some instances. The level of corrosion with the CTFE was approximately similar to that of the unformulated fluid, and a more detailed discussion is provided in association with Fig. 8.

2. Oxidation-Corrosion Tests at 175°C

Measurements taken during oxidation-corrosion tests at 175°C with the formulated oils are shown in Fig. 6. No high temperature oxidation-corrosion tests were performed with the Dow Corning silicone fluid, as its stability characteristics are likely to be similar to that of the MIL-B-46176 silicone fluid. In addition, the thermal and oxidation characteristics of most silicone fluids are normally considered to be good.⁽¹¹⁾

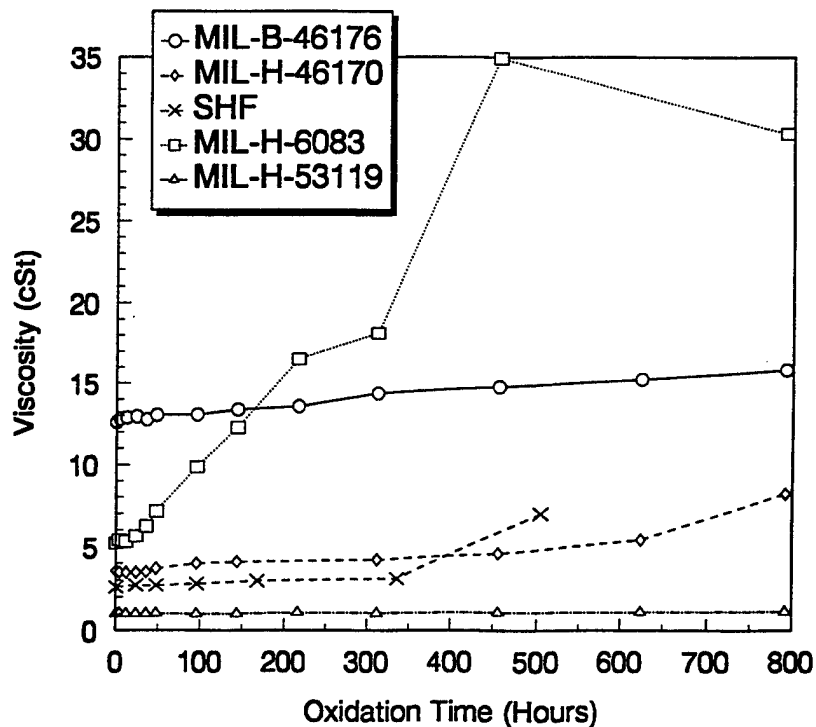


a. Kinematic viscosity at 100°C

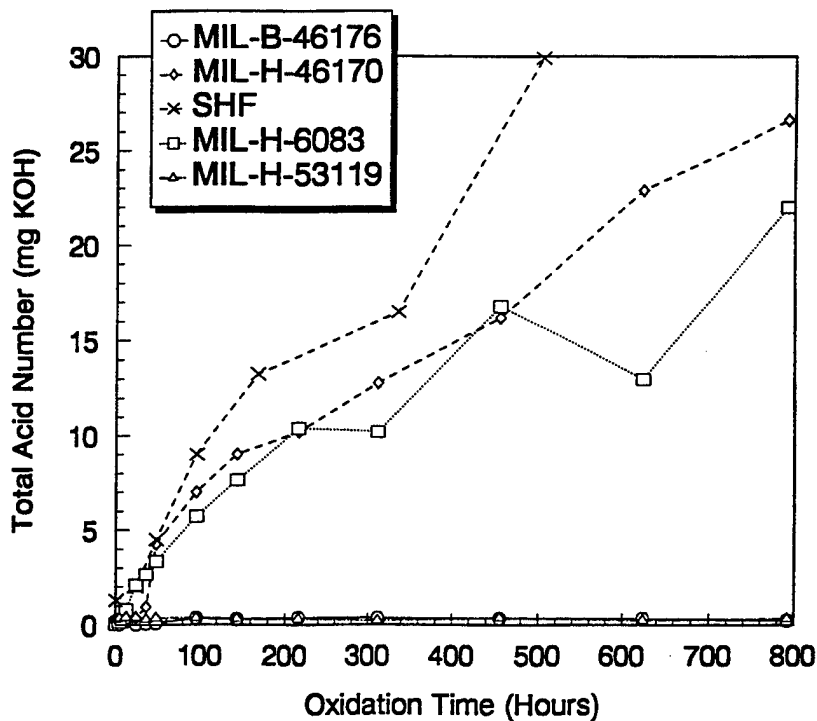


b. Total Acid Number

Figure 5. Oil degradation measured during oxidation-corrosion tests with formulated oil performed according to ASTM D 4636 at 135°C



a. Kinematic viscosity at 100°C

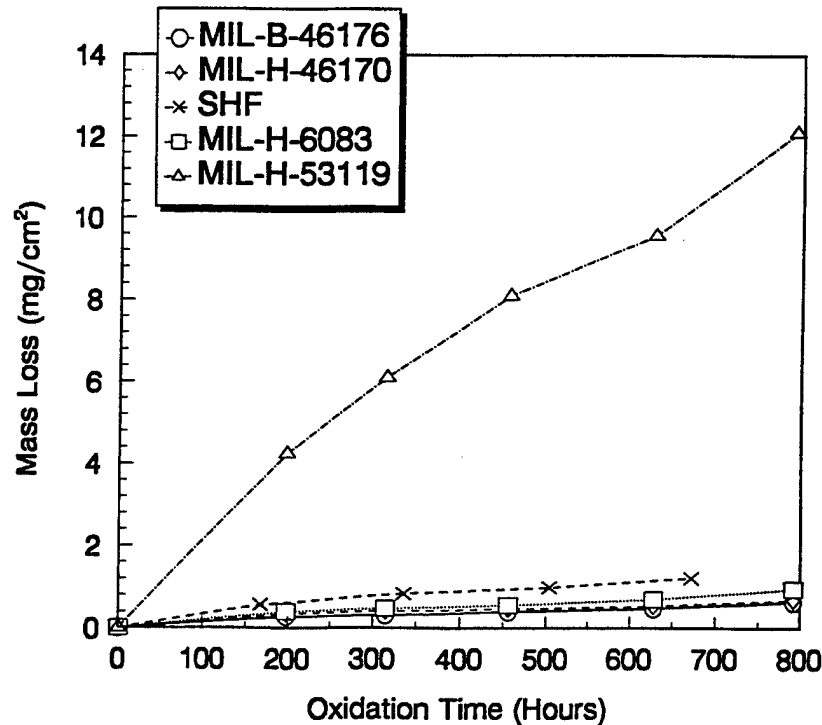


b. Total Acid Number

Figure 6. Oil degradation measured during oxidation-corrosion tests performed according to ASTM D 4636 at 175°C

As was observed at lower temperatures, the petroleum- and PAO-based oils are less stable than the remaining fluids, and a significant increase in TAN is immediately evident. The kinematic viscosity of the petroleum-based oil was also affected. By comparison, the TAN of the formulated silicone and CTFE fluids remained unchanged, although in previous work (6) at higher temperatures (302°C), the CTFE fluid experienced increased acid number and viscosity, especially in the presence of Cu, Fe, Mn, Sn, Ti, and Zn. Samples of the new and degraded CTFE fluid were also examined using FTIR and GC. No variation was observed between the FTIR spectra of new oil and oils oxidized at 175°C, as shown in Figs. D-1 and D-3, respectively. However, considerable variation is apparent from the gas chromatograms shown in Fig. F-1, indicating that some change in composition has occurred during the severe oxidation environment.

The C-93200 bronze metallurgy was susceptible to corrosion by each of the fluids at 175°C, as shown in Fig. 7 (the results obtained for the remaining metallurgies are provided in Fig. A-3). Especially severe corrosion was present for the CTFE fluid, despite a stable TAN. The material removal rate in CTFE was approximately constant and approached 0.015 mg/cm²hr (1.9×10^{-6} cm/hr), compared to approximately 0.001 mg/cm²hr for the remaining fluids [the results are plotted as cumulative mass loss (mg/cm²)]. SEM micrographs of the new and corroded C-93200 are included in Appendix B and show a severely pitted topography. CTFE also produced more severe corrosion on the NR955 copper alloy than the remaining fluids, but was significantly less than observed with C-93200, at approximately 0.0005 mg/cm²hr. The 4140 steel was almost unaffected by CTFE (Fig. A-3), but received a sapphire blue coating in the silicone-based fluid [previous workers have noted similar films (22)]. The relatively high acid numbers of the petroleum- and PAO-based oils did not produce very severe corrosion with any metallurgy compared to CTFE qualified under MIL-H-53119. The low viscosity single hydraulic fluid (SHF) produced marginally higher acid numbers than the regular PAO fluid under these severe conditions, with acid number changes beginning immediately after test initiation for both fluids. This increased acidity produced some corrosion of the NR955 copper-based material, as shown in Fig. A-3. However, as previously stated, the material removal rate was appreciably less than that seen between CTFE and the C-93200 bronze, shown in Fig. 7.



(Note: The results for the remaining metallurgies are provided in Appendix A.)

Figure 7. Mass loss measured on C-93200 bronze during oxidation-corrosion tests with fully formulated fluids at 175°C

Additional tests were performed at 145 and 160°C with the CTFE fluid qualified under MIL-H-53119 to define the effects of temperature on corrosion rate. TAN and viscosity were not measured at these intermediate temperatures, as no variation in these characteristics was previously observed for the MIL-H-53119 fluid after 800 hours at 175°C. The mass loss measured at each temperature is plotted in Fig. 8 as a function of oxidation time. As expected, the reaction rate between the bronze specimens is a nonlinear function of temperature and increases dramatically between 160 and 175°C. In each instance, the corrosion process is a linear function of time, with no initiation period required to deplete natural or artificial inhibitors.

The used CTFE fluid from the oxidation-corrosion test had a discoloration ranging from yellow to red, depending on the test temperature, and it contained a relatively low density black insoluble product that settled at the surface of the fluid. The used fluids from the lower temperature tests were more discolored than those from the higher temperature tests. X-ray

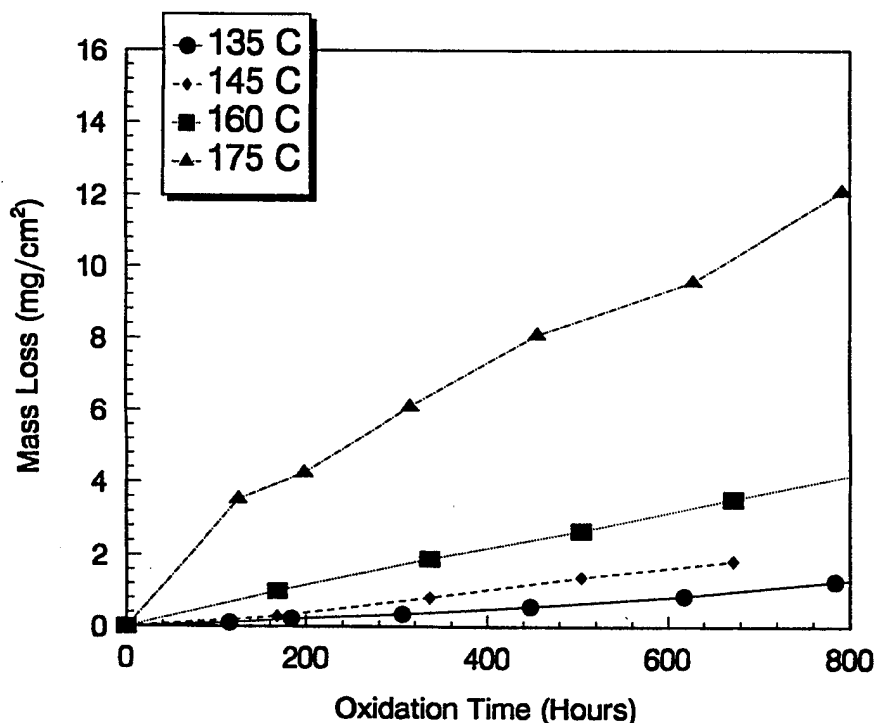


Figure 8. Corrosivity of MIL-H-53119 on C-93200 high-lead tin bronze at various temperatures

fluorescence revealed traces of bromine in the CTFE fluid and an increased concentration in the black insoluble corrosion product. A more detailed discussion of this analysis will be provided in the next section.

The results of oxidation-corrosion tests performed with copper, tin, lead, and zinc (>99.5 percent pure), which are the primary constituents in C-93200 bronze, are provided in Fig. A-4. Severe corrosion of each specimen was observed. Indeed, at 135°C, the material removal rate from the individual elements was one to two orders of magnitude greater than that seen with the C-93200 material. More severe corrosion was present at 175°C; however, the overall rate was now similar to that of the C-93200 material.

3. Corrosion Tests in an Oxygen-Free Environment

The rate of degradation for conventional hydrocarbon fluids is highly sensitive to the availability of both oxygen and moisture. However, the severely aged CTFE fluid showed no increase in either acid number or viscosity, as would be expected for a conventional hydrocarbon. As a

result, the previously detailed high-temperature corrosion test was repeated in a nitrogen atmosphere. These test conditions simulate use of the hydraulic fluid in a fully sealed environment devoid of oxygen. Test coupons of C-93200 bronze were immersed in CTFE hydraulic fluid for a period of 500 hours at test temperatures of 135 and 175°C. The remaining test parameters, including gas (nitrogen) flow rate, remained unchanged from the preceding tests.

The mass loss per unit area of the C-93200 specimens in nitrogen is plotted in Fig. A-5, along with comparable results obtained in air. Material removal is significantly reduced by the elimination of oxygen at both 135 and 175°C. Some corrosion was observed at 175°C during the first 100 hours of testing, probably due to residual oxygen in the oil. The rate of material removal decreased significantly toward the end of the test.

B. Chemical Analysis of Corrosion Mechanism

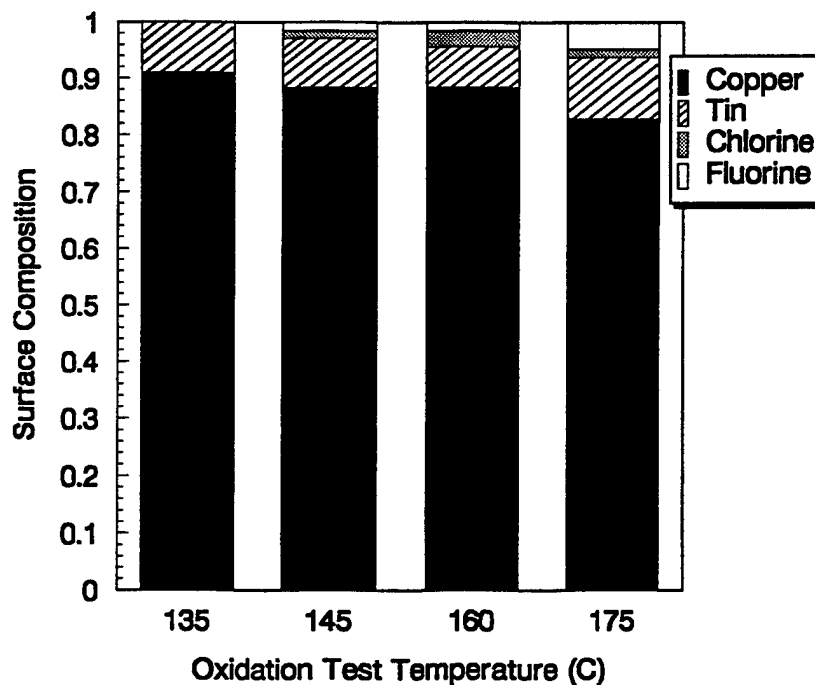
1. Surface Chemical Analysis

Surface chemical analysis was performed using AES to define the effects of CTFE on C-93200 high leaded tin bronze. Initial analysis concentrated on the surfaces of metal coupons from oxidation tests, which were performed at a range of temperatures previously illustrated in Fig. 8. Auger analysis was performed on a "new" specimen that had been immersed in CTFE at room temperature to simulate the effects of unreacted CTFE remaining after the cleaning process. Auger analysis was also performed on wear scars formed during Cameron-Plint tests at a range of temperatures at the conditions detailed later in TABLE 6. A duplicate analysis was taken on the surface of the wear test specimens just outside the contact area to precisely define the effects of wear. Simple analysis of the surfaces is clouded by the presence of unintentional contaminants such as carbon and oxygen.

The effects of carbon and oxygen contaminants were reduced by gradual removal of the surface by ion sputtering, as shown in Figs. C-1, C-2, and C-3. The data obtained on the as-received or new sample show that ion beam sputtering to 33-angstrom depth removed most of the carbon and oxygen. At 33 angstroms, Cu was the dominant element, with small amounts of Sn and Zn also

detected. At 100-angstrom depth, the amounts of carbon and oxygen present were further reduced, with Cu remaining dominant. In the case of C-93200 bronze corroded by hot CTFE, ion beam depth profiling to 33 and 100 angstroms greatly reduced the amounts of carbon and oxygen detected, but not as significantly as was observed in the "new" sample case, indicating strong adsorption or bonding of carbonaceous and oxygenated species to the bronze surface.

The relative concentration of the principal elements present on the surface of the oxidation test specimens exposed to CTFE at 135, 145, 160, and 175°C is shown in Fig 9. The surfaces have been sputtered to a depth of 30 angstroms and ignore any contaminants such as carbon and oxygen which remain after the sputtering process. No evidence of lead or zinc is present at the surface of either the new or corroded specimens⁵, and more copper than tin is removed from the bronze surface as the CTFE corrosion temperature is increased. Previous oxidation-corrosion tests (shown in Fig. A-4) indicated relatively severe corrosion of elementally pure copper, lead,



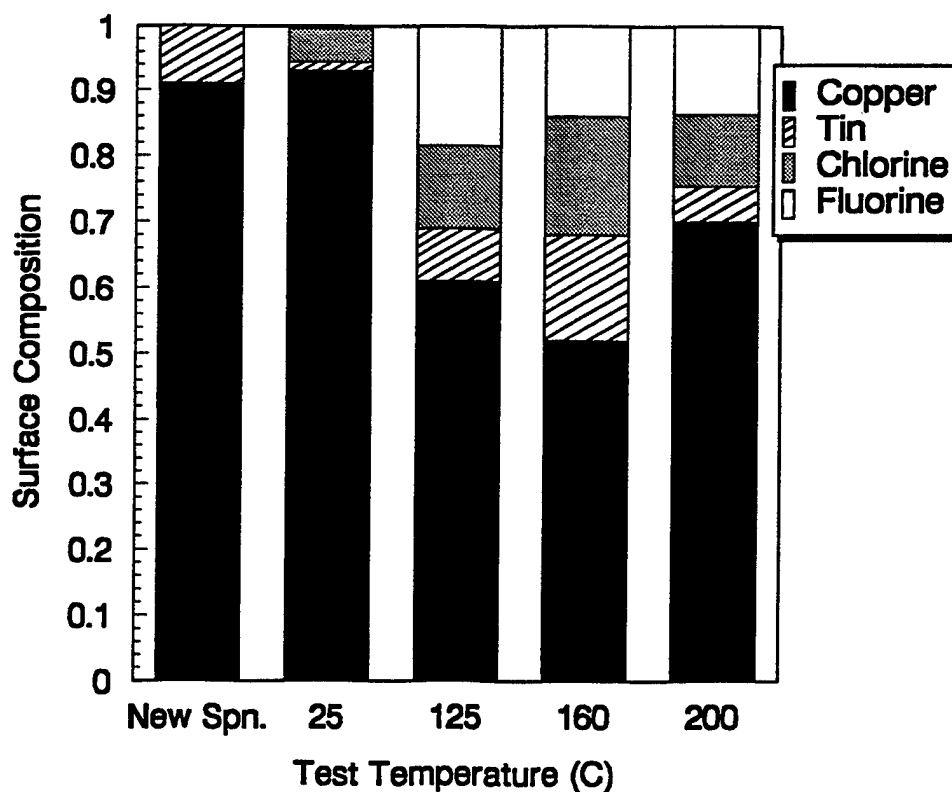
(Note: Results exclude contaminants such as carbon and oxygen.)

Figure 9. Surface composition of C-93200 bronze specimens from oxidation-corrosion tests at a sputtered depth of 33 angstroms

⁵ The elemental composition of the C-93200 high-leaded tin bronze is 83 percent Cu, 7 percent Sn, 7 percent Pb, and 3 percent Zn.

tin, and zinc at temperatures as low as 135°C. The ability of CTFE to corrode each of the major elements in bronze may explain the composition changes observed in the corroded bronze material.

Traces of chlorine and fluorine are present on the surfaces from both the corrosion and wear tests. In each instance, the effect is temperature-dependent, and neither fluorine nor chlorine is present on specimens immersed in the fluid at room temperature. The amount of fluorine increases more rapidly than chlorine as the CTFE corrosion temperature is increased. The source of the fluorine could be from CTFE, the fluorinated sulfonamide antiwear additive, or both. In addition, the concentration of both chlorine and fluorine is increased by the wear process, as summarized in Fig. 10. The fluorine concentration outside the wear scar (not shown) was similar to that of the specimens from the oxidation-corrosion test. It should be noted that the new specimen was immersed in CTFE fluid prior to analysis to simulate the effects of unreacted CTFE residue remaining from the surface cleaning process.



(Note: Results exclude contaminants such as carbon and oxygen.)

Figure 10. Surface composition of C-93200 material within a wear scar produced during tests lubricated with CTFE

Analysis indicates differing surface reactions are present as temperature is increased. At 175°C, the amount of carbon detected on the surface was about 35.8 surface atomic percent, a dramatic reduction from the 76 percent and 58 percent found in the ambient and 135°C treated bronze specimens, respectively. However, the amount of surface carbon in oxidized form (C-O type bonding) was much increased in the 175°C exposed specimen in contrast to the 135°C and ambient cases, which showed only a small trace of carbon in an oxidized form. The XPS data also showed a progressive increase in the surface-bonded oxygen from 16.2 surface atomic percent at ambient to 30.3 surface atomic percent at 175°C.

The XPS data for the ambient, 135°C, and 175°C CTFE-exposed bronze surfaces showed an interesting trend in the total surface atomic percent nitrogen found. The respective values, 0.4 percent (ambient), 3.4 percent (135°C), and 7.0 percent (175°C) show an increase in surface bound nitrogen (indicated to be in an organic form). This could reflect surface bonding of the fluorinated sulfonamide antiwear additive or of its thermal or thermo-oxidative decomposition product.

Surface analysis from high resolution XPS spectra showed that the metallic constituents on the surface of the bronze specimen were present in an oxidized form over the complete temperature range, with Cu_2O , SnO_2 , and PbO forms present. However, at 175°C, SnO , PbF_2 , and PbCl_2 are probably also present. Similarly, no surface fluorine was detected in the ambient and 135°C cases, increasing to about 6 atomic percent at 175°C. The surface fluorine was present in both an inorganic (F^-) form as well as the dominant organic form (related to CTFE and its decomposition products). The amount of chlorine increased from 0.2 surface atomic percent at ambient to approximately 1 atomic percent (in an inorganic form) at 175°C. Other workers have observed similar effects with these fluids. Gupta and coworkers (6) found evidence of CuCl using X-ray diffraction and X-ray fluorescence in the vicinity of copper specimens corroded by CTFE. Similarly, Reference 23 found no chlorine on bronze specimens immersed in CTFE at low temperatures using Energy Dispersive X-ray (EDX), but chlorine concentrations of up to 26 percent were present at 175°C.

As previously stated, the used CTFE fluid from the corrosion test had a discoloration ranging from yellow to red (depending on the test temperature), and it contained a relatively low density black insoluble product that settled at the surface of the fluid. The used fluids from the lower temperature tests were more discolored than those from the higher temperature tests. The discoloration appeared to be precursors to the black insoluble product formed by the corrosion process. It is envisioned that the used CTFE fluid produced at the higher temperature is clearer because the precursors decomposed more completely to form the black insoluble product.

X-ray fluorescence revealed traces of bromine in the hydraulic fluid and at increased concentrations in the black insoluble corrosion product. Bromine appears to be an impurity that probably was present in one of the raw materials, such as the chlorine used in the synthesis of the hydraulic fluid. If that is the case, the bromine would be bonded to the fluid in the form of a bromotrifluoroethylene polymer. Both the used and the virgin fluid contained about 40 ppm of bromine. The black insoluble product contained about 100 ppm of bromine, significant amounts of zinc and copper, and a trace of chlorine. The black insoluble product appears to be an oxy-fluorocarbon containing small amounts of heavier elements such as copper, zinc, bromine, and chlorine entrapped in the structure. The product has a lower density than that of the CTFE hydraulic fluid.

2. Corrosion Mechanism

A definitive description of the high temperature corrosion mechanism present between CTFE and bronze has not been achieved. However, it is likely that the corrosion process is initiated by the breaking of C-Br and C-Cl bonds in the hydraulic fluid. The trace quantity of bromine in the fluid may play a disproportionate role in the corrosion mechanism due to the relatively low bond energy of the C-Br bond [the bond dissociation energies of the halocarbons decrease in the order $D(C-F) > D(C-Cl) > D(C-Br) > D(C-I)$]. Furthermore, increased concentrations of bromine are present in the reaction products. The corrosion process seems to be driven by a metal-catalyzed auto-oxidation reaction in which a free radical mechanism is initiated by breaking chemical bonds. The corrosion process may be initiated when a bromine derivative of the hydraulic fluid reacts with the metal (M), as follows:



Reaction 1 forms a chlorofluorocarbon radical that in Reaction 2 combines with oxygen to form a chlorofluorocarbon peroxy radical. In Reaction 3, the peroxy radical reacts with metal to form a metal oxide.



The chlorofluoro-oxy radical produced in Reaction 3 decomposes into a stable oxy-chlorofluorocarbon and a chlorine atom. In Reaction 5, the Cl atom reacts with oxygen to form a chloro-peroxy radical,



which in Reaction 6 produces more metal oxide.



The ClO radical may react in several ways to continue the chain reaction.

In summary, chlorine and bromine in the hydraulic fluid are likely to be the main cause of corrosion, as they are less strongly bonded to carbon in the fluid than is fluorine. Since the C-Br bond strength is the weakest, bromine contamination of the fluid may significantly enhance the corrosion rate. Additional oxidation-corrosion tests using a CTFE fluid free of bromine are required to confirm the proposed corrosion mechanism.

C. Wear Tests

1. Four-Ball Wear Test According to ASTM D 4172

MIL-H-53119 (10) and MIL-H-6083 (1) specify maximum wear scar diameters of 0.8 and 1 mm, respectively, in four-ball wear tests performed according to ASTM D 4172. Fluids that produce a scar below this value should provide acceptable wear protection within conventional hydraulic systems. However, it should be noted that such applications typically are governed by the extreme pressure (EP) properties of the fluid. EP characteristics are likely to be less relevant to the gun recoil brake mechanism, which typically consists of conformal contacts of softer metallurgy.

Each of the oils, except for those derived from a silicone base, produced acceptable wear in the ASTM standard test (as detailed in TABLE 4). MIL-B-46176 (12) specifies no minimum wear resistance for the silicone fluids. Fully formulated CTFE produced a wear scar of 0.61mm, which is in good agreement with previous studies in this area.(7) Unexpectedly mild wear was observed for the unadditized CTFE fluid. Indeed, neat CTFE produced marginally less wear than the fully formulated oil in the highly repeatable four-ball wear test. This result is contrary to previous work that reported four-ball wear scars of up to 2.6 mm with broadly similar unformulated CTFE fluids.(7) No explanation for this result is apparent. FTIR spectra for the

TABLE 4. Results of Four-Ball Wear Tests Performed According to ASTM D 4172

| <u>Fluid Specification No.</u> | <u>Wear Scar Diameter, mm</u> |
|--------------------------------|-------------------------------|
| MIL-H-6083 | 0.64 |
| MIL-H-46170 | 0.38 |
| Single hydraulic fluid | 0.58 |
| MIL-B-46176 | 1.75 |
| MIL-H-53119 | 0.61 |
| MIL-H-53119 (Basestock) | 0.56 |
| Dow Corning Silicone | 2.10 |

basestock and formulated fluids were also very similar, as shown in Appendix D, although the additive concentration may not be sufficient to register using this technique. An independent reference spectrum for either the neat or formulated CTFE fluid was not available to the TARDEC Fuels and Lubricants Research Facility (TFLRF).

2. Cameron-Plint Tests Performed on Conformal Test Specimens

Initial wear tests were performed using the test specimens machined from sections of the full-scale component, i.e., contacts A, B, and C in TABLE 2. In each instance, a conformal contact is produced, the area of which does not vary throughout the complete test duration. To ensure accurate alignment, an initial running-in period of 15 minutes was performed prior to each test at half the final test loading. This procedure ensures that the load is evenly distributed over the apparent contact area, thereby minimizing the effects of random misalignment. As previously stated, the contact conditions in practical operation are likely to vary over a broad range and have not been defined. As a result, widely differing contact conditions (especially pressure) were used in each laboratory test series, as detailed in TABLE 5, to provide a broad range of likely wear mechanisms.

TABLE 5. Contact Conditions Used in Generation of Test Results Plotted in Fig. 11

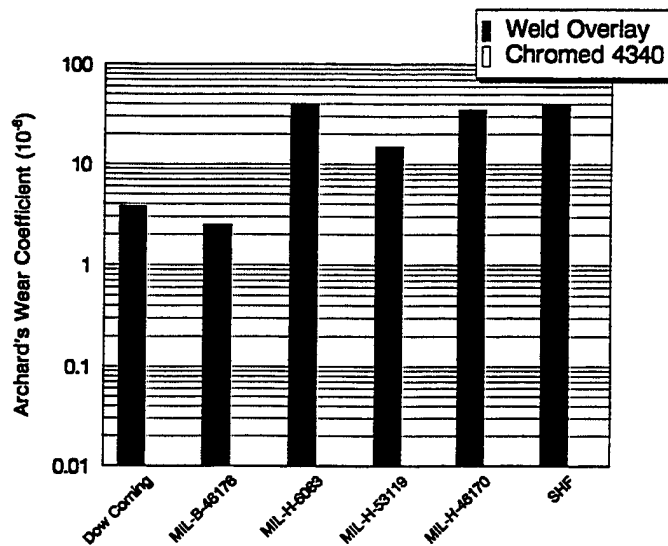
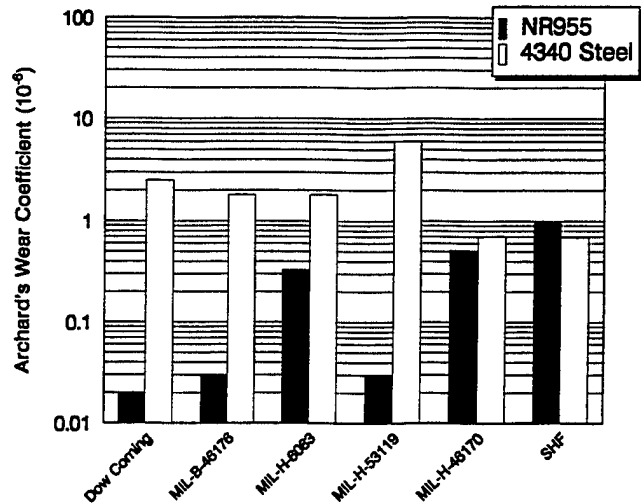
| Parameter | Contact | | |
|-------------------------------|---------|-------|-------|
| | A | B | C |
| Speed, Hz | 30 | 20 | 20 |
| Speed, mm/s | 285 | 190 | 190 |
| Load, N | 100 | 20 | 20 |
| Pressure, Pa | 46 | 2.09 | 10.6 |
| Temperature, °C | 120 | 80 | 80 |
| Duration, min | 180 | 100 | 100 |
| Amplitude, mm | 4.76 | 4.76 | 4.76 |
| Contact Area, mm ² | 2.156 | 9.525 | 1.886 |

The results of the conformal wear tests with contacts A, B, and C are plotted in Fig. 11. The wear volume was derived from a measure of the total mass loss from the specimens and surface profiles taken using the Talysurf. In each instance, Archard's wear coefficient is plotted on a logarithmic scale and ranges over several orders of magnitude. For the total test duration used, a wear coefficient of 0.02 is approaching the minimum resolution of the test equipment. As a result, no measurable wear was present on the chrome-coated 4340 specimen sliding on the relatively soft weld overlay.

Few strong trends are apparent. Surprisingly severe wear was observed for the 4340 steel sliding on NR955, although the difference in hardness between the metals is accounted for when the results are normalized using Archard's wear coefficient. Clearly, this simple equation is not sufficient to account for the widely varying test conditions used. In general, the nonflammable CTFE fluid qualified under MIL-H-53119 produced similar wear to both the PAO- and petroleum-based liquids. Moreover, the viscosity of the CTFE is less than the remaining oils, minimizing fluid film lift. Uncharacteristically mild wear was observed for both silicone-based oils, compared with the preceding four-ball tests (see TABLE 4). However, the four-ball configuration produces a highly loaded concentrated contact that minimizes thick film lubrication. In contrast, the relatively high viscosity and viscosity index of the silicone oils (see TABLE 1 and Fig. 1) will promote hydrodynamic lift with the present conformal contact geometry. Indeed, silicone fluids are normally considered highly desirable hydrodynamic lubricants with poor boundary lubrication characteristics.⁽²⁴⁾

Cameron-Plint wear tests with the conformal specimens lubricated with the unadditized basestock fluids gave directionally similar results to those obtained using the four-ball wear test and are not reprinted. Both the petroleum and PAO basestock fluids produced more severe wear than the formulated product. In contrast, the basestock for the CTFE fluid again produced slightly less wear than the fully formulated oil.

a. Contact Type A



b. Contact Type B

c. Contact Type C

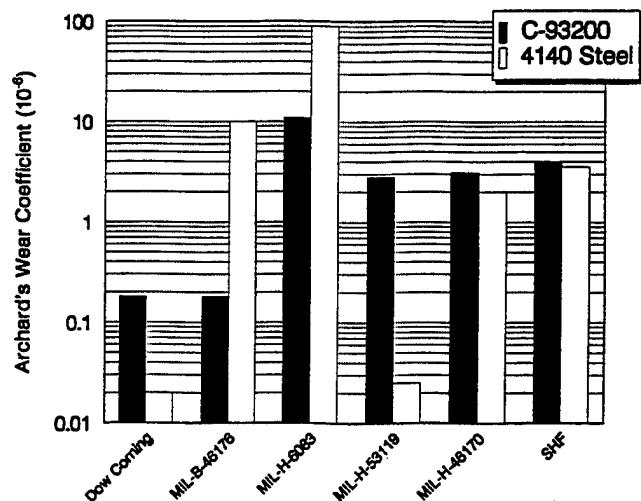


Figure 11. Wear test results obtained with conformal contacts at contact conditions defined in TABLE 5

3. Cameron-Plint Tests Performed on Counterformal Specimens

In the preceding section, laboratory wear tests were performed with conformal specimens under relatively low apparent contact pressures. The conformal geometry has a number of disadvantages:

- a. Accurate wear measurement under such conditions requires an extended test duration, greatly limiting the number of tests that may be performed.
- b. The need for precise specimen alignment further reduces test repeatability and necessitates a running-in period.
- c. The conformal geometry is susceptible to fluid film lift, masking the intrinsic boundary lubricating qualities of the fluid.

The above disadvantages necessitated development of a standardized counterformal contact geometry. This configuration allows accurate measurement of the wear scar diameter using optical microscopy and subsequent calculation of the corresponding wear volume. The oxidation-corrosion tests reported in Section V-A indicate that the C-93200 high-leaded tin bronze is more susceptible to the effects of oil degradation than the remaining metallurgies considered. As a result, the counterformal test specimen was manufactured from this material, as previously described in TABLE 2.

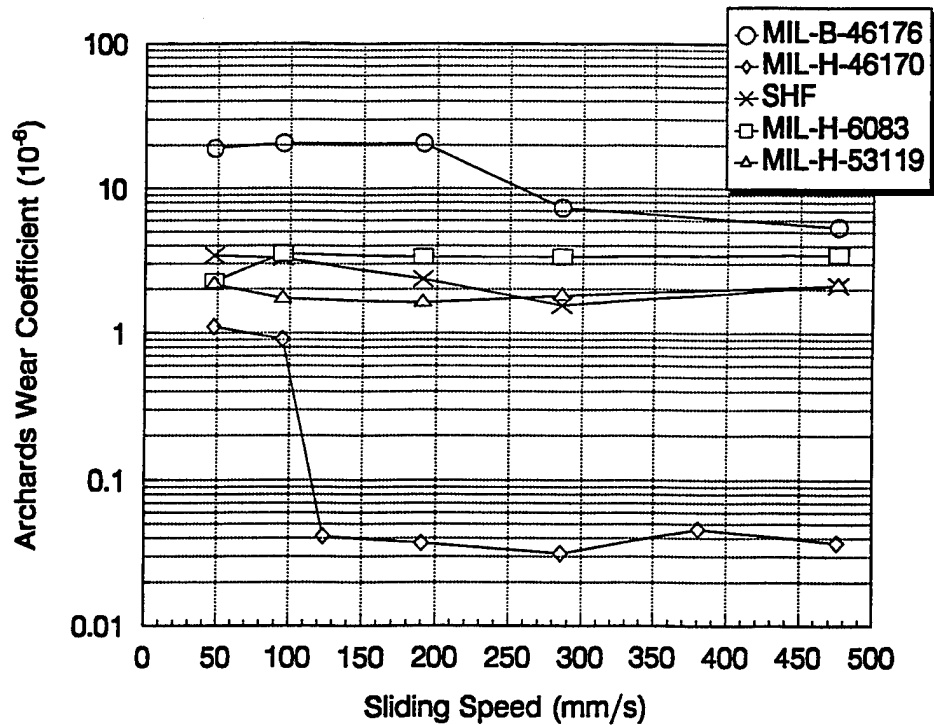
The variables considered during subsequent wear tests with counterformal specimens include applied load, sliding speed, temperature, and cumulative oxidation-corrosion test hours. Typically, all but one of the parameters remained constant at the conditions defined in TABLE 6. The remaining parameter was then varied to define its effect on the level of friction and wear associated with each fluid. No tests were performed using the silicone fluid manufactured by Dow Corning due to its relatively high viscosity of 30 cSt, which makes it especially susceptible to hydrodynamic lift. In addition, the results of preceding sections indicate that its characteristics are broadly similar to those of the second silicone-based oil, qualified under MIL-B-46176.

TABLE 6. Contact Conditions Used in Wear Tests With Counterformal Contacts

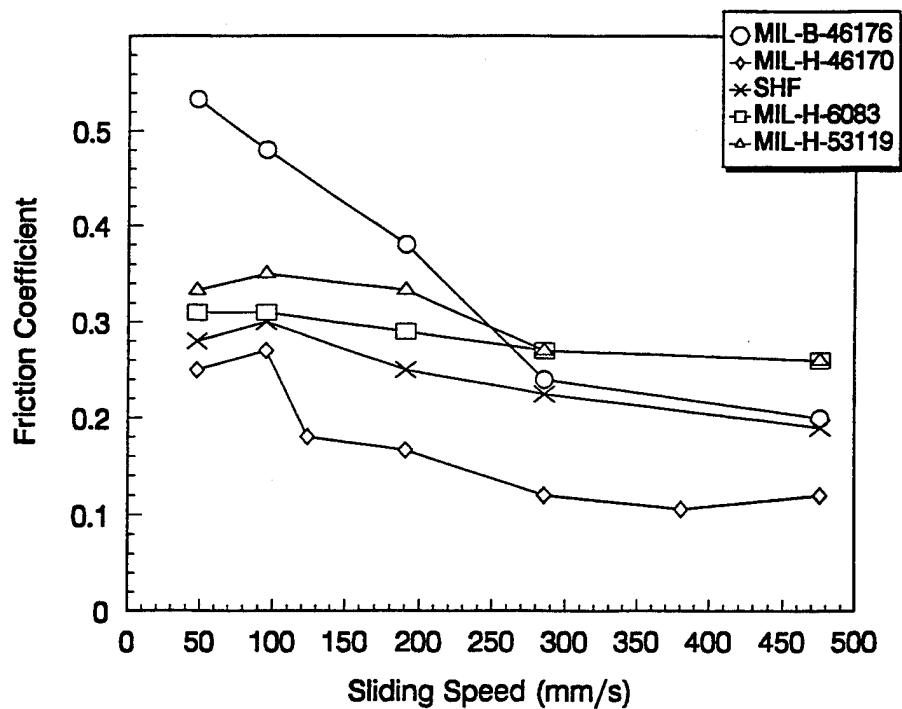
| Parameter | Value |
|-------------------------------|--|
| Speed, Hz | 5 |
| Speed, mm/s | 50 |
| Load, N | 75 |
| Pressure, Pa | 75/(Contact Area) |
| Contact Area, mm ² | $\pi \times (\text{Wear Scar Diameter}/2)^2$ |
| Temperature, °C | 125 |
| Duration, min | 30 |
| Amplitude, mm | 4.76 |
| Sliding distance, mm | 85,680 |

Initial wear tests were performed using the counterformal geometry to define the effects of sliding speed (and hydrodynamic lift) on wear rate. The total test duration was adjusted along with sliding speed to produce a constant sliding distance of 342 m, which is distinct from the standardized conditions reported in TABLE 6. The normalized wear rate and mean friction coefficient during tests with each of the above oils are plotted in Fig. 12 as a function of sliding speed. Overall, the CTFE fluid produced less wear than the baseline petroleum oil qualified under MIL-H-6083 and the low viscosity PAO-based single hydraulic fluid. A significant decrease in wear rate was observed for the higher viscosity PAO-based MIL-H-46170 oil at a sliding speed above 100 mm/s. The decrease may be partially due to hydrodynamic lift, although a comparable decrease was not observed for the MIL-H-6083 fluid, which has similar viscosity. The reduction in wear with CTFE may be partially attributed to surface reaction due to high flash temperatures within the contact junction.⁽²¹⁾ The effects of increasing speed and hydrodynamic lift are apparent from the measured friction coefficient, especially for the higher viscosity oil. As a result, all subsequent wear tests were performed at a mean sliding speed of 50 mm/s, which is the minimum available.

Intermediate samples of degraded oil were available from the previously described oxidation-corrosion test at 175°C. The results of Cameron-Plint wear tests performed at 125°C with each of the oils are plotted in Fig. G-1. A slight increase in wear rate was observed as the oxidation



a. Normalized wear rate



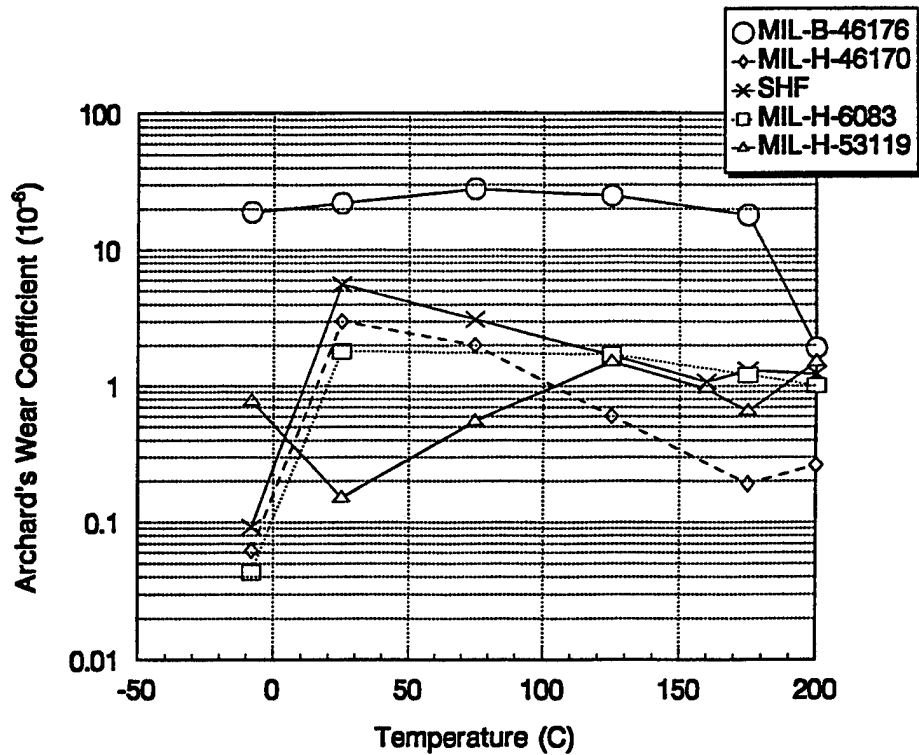
b. Friction coefficient

Figure 12. Effect of sliding speed on C-93200 contact

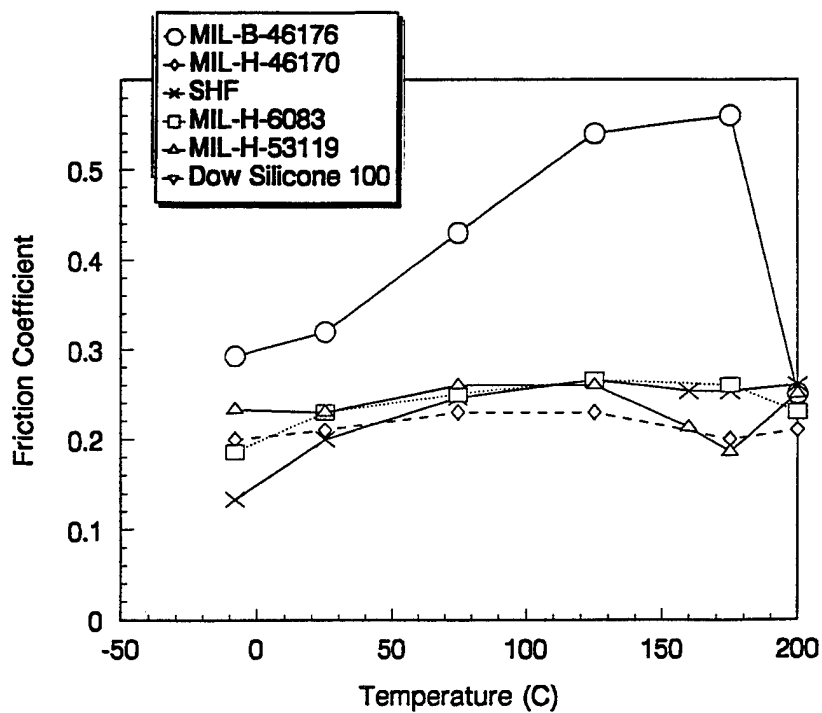
time of the CTFE fluid increased, possibly due to the formation of corrosive products within the oil. In contrast, a significant decrease in wear rate was observed for the MIL-H-6083 fluid due to its rapidly increasing viscosity, as shown in Fig. 6a. A concomitant decrease in friction was also observed.

Examination of the wear scar topography using an optical microscope indicated some adhesive transfer from the softer bronze specimen at all temperatures. However, results provided in preceding sections indicate a strong chemical reaction between chlorine compounds (from the CTFE) with C-93200, the severity of which increases disproportionately with temperature. Chlorine compounds are occasionally added to lubricants to act as an extreme pressure agent and react with the rubbing surface at elevated temperatures, produced by either ambient conditions or else by frictional heating.⁽¹¹⁾ This process may be most effective under highly loaded conditions, such as those used in the present counterformal contact, but may promote the previously described corrosive wear under more lightly loaded conditions less prone to adhesive welding. To better define this effect, wear tests were performed to define the possible effects of increasing temperature, mechanical contact, and surface corrosion on material removal. These tests were performed using Contact D in new oil unless otherwise specified, with the results plotted in Figs. 13 and 14.

Fig. 13 shows normalized wear rate as a function of temperature, with the remaining test conditions defined in TABLE 6. In general, wear rate with the CTFE fluid increases with temperature. This result is unlikely to be solely due to decreased hydrodynamic lift, as no such effect is observed for the remaining oils, some of which are more viscous. At higher temperatures, the trend is temporarily reversed, and both friction and wear decrease, reaching a minimum at approximately 175°C. This decrease is repeatably accompanied by the formation of a strong contact resistance, confirming the presence of an effective chemical boundary film. Wear rate with the CTFE fluid increased at temperatures below ambient, possibly due to

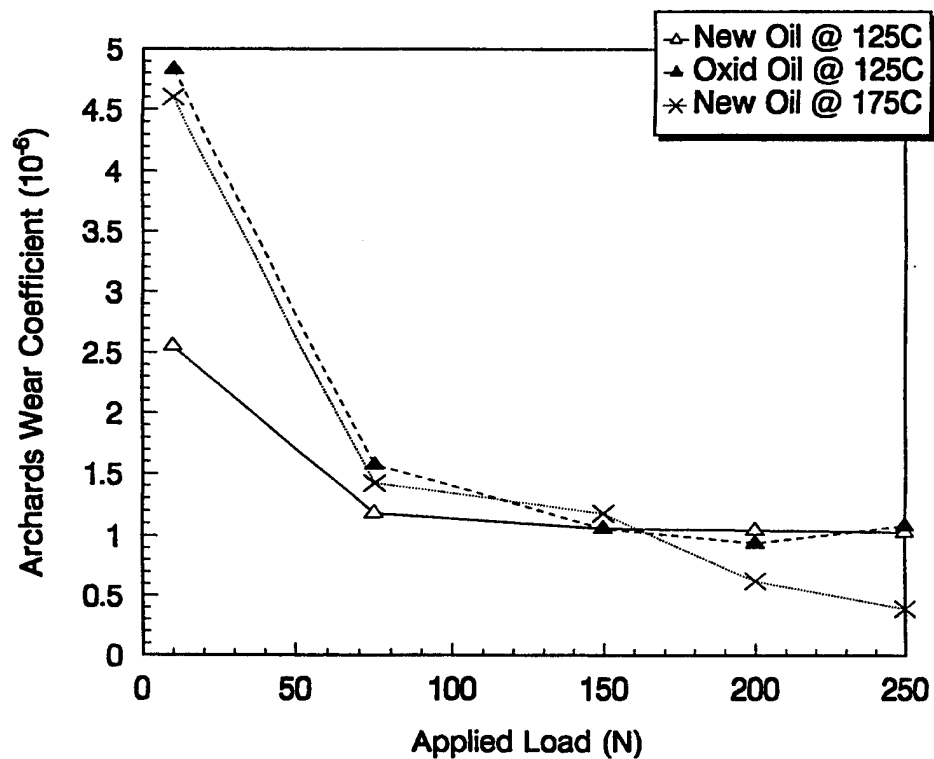


a. Normalized wear rate

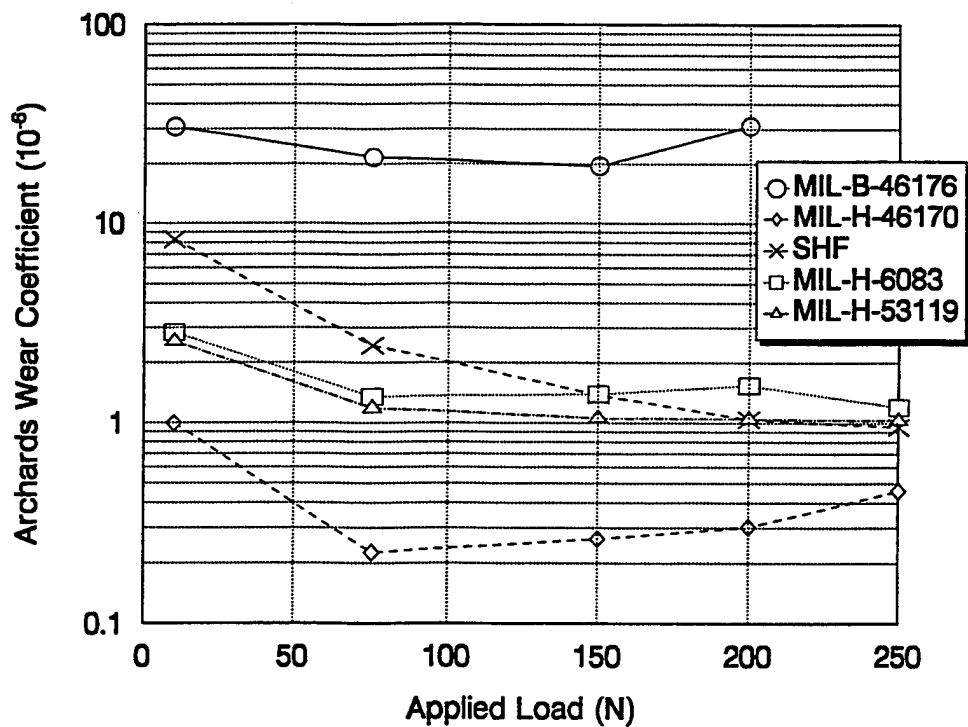


b. Friction coefficient

Figure 13. Effect of operating temperature on C-93200 contact



a. New fluids tested at 125°C



b. New and degraded CTFE fluid

Figure 14. Effect of applied load on C-93200 contact

formation of small amounts of condensation in the test reservoir⁶. Overall, however, the wear rate with CTFE was similar to that of the remaining fluids, except for MIL-B-46176, which produced very high wear over the complete temperature range. Slightly higher wear was produced by the low viscosity single hydraulic fluid over the complete temperature range when compared to the regular PAO oil. A general decrease in wear rate was observed at very low temperatures for many of the fluids, possibly due to increased hydrodynamic lift.

The effects of applied load on the measured wear rate with each of the test fluids are plotted in Fig. 14a. The friction coefficient is not plotted due to decreased accuracy of the force measurement apparatus at very low loads. In general, a slight increase in the **normalized** wear rate is observed for each of the fluids at low loads. This result indicates that the normalized wear rate at low loads was greater than that predicted to exist from consideration of contact forces alone (the true wear volume still decreased at low loads). It should be noted that in each instance, the measured wear scar diameter was appreciably greater than the calculated Hertzian contact diameter, as detailed in Fig. 4. The results of additional wear tests with degraded CTFE fluid at 125°C as well as new oil at 175°C are shown in Fig. 14b (the normalized wear rate is not plotted using a logarithmic scale in this instance). The previously noted relationship between decreasing contact stress and wear rate is increased by preoxidation of the oil or increased contact temperatures. Once again, a stronger contact resistance is observed at high temperatures. The chemical nature of the film has not been defined but is probably related to the surface corrosion of the bronze material by CTFE, which occurred at similar temperatures. Such corroded surface layers may increase wear rate at low loads while acting as an EP agent at higher loads, although the tribological characteristics of the CTFE-induced film are also not yet defined.

⁶ Reference 6 indicates that the presence of moisture in CTFE greatly accelerates the corrosion rate of copper. In addition, the reaction mechanism is altered by moisture to form copper compounds that are more soluble in CTFE. It is unlikely, however, that an appreciable volume of moisture will be available to the oil in the gun recoil mechanism.

D. Evaluation of Surface Treatment Procedures for C-93200 Bronze

1. Background to Surface Treatment Evaluation

The data reported in the previous sections indicated that CTFE fluid provides good wear resistance but will cause corrosion of C-93200 bronze at high temperatures. This section evaluates the surface treatment processes summarized in TABLE 7 when applied to C-93200 bronze immersed in CTFE hydraulic fluid. It is recognized that using such a coating may eliminate many of the benefits associated with use of the bronze metallurgy.

TABLE 7. Surface Treatment Procedures Evaluated in This Study

| Trade Name | Manufacturer | Treatment Type | Thickness, $m \times 10^{-6}$ | | Attributes | Hardness, Rc |
|-----------------|--------------------|------------------------------|-------------------------------|-----------|-------------------------|--------------|
| | | | Range | Tol. | | |
| NEDOX SF-2 | General Magnaplate | Nickel/Polymer | 5-75 | ± 5.0 | Friction/Wear/Corrosion | 65 |
| Chromion | Beamalloy | IBD* Chrome | 2-3 | -- | Wear/Corrosion | 82 |
| -- | -- | Chrome | ≈ 25 | -- | Wear/Corrosion | 30 |
| AeroNikl 250 | Sifco | Sulfamate Nickel | 10-15 | ± 2.5 | Corrosion | 22 |
| Magnagold | General Magnaplate | PVD† Titanium Nitride | 1-3 | ± 0.5 | Friction/Wear | 85 |
| CF _x | Wear Cote | Modified electroless nickel‡ | 30 | ± 2.5 | Wear/Corrosion | 70 |

* = Ion Beam-Deposited

† = Physical Vapor Deposition

‡ = Composite electroless nickel containing fluorocarbon particles (not PTFE)

The PVD Titanium Nitride did not adhere to some of the wear test surfaces, possibly due to the presence of slight surface finish; irregular discoloration of the treated surfaces was apparent even at room temperature. No difficulty was encountered during application of this process to the test coupons intended for use in the oxidation-corrosion test, possibly because of their low surface roughness. Many of the surface treatment processes are intended to provide both wear and

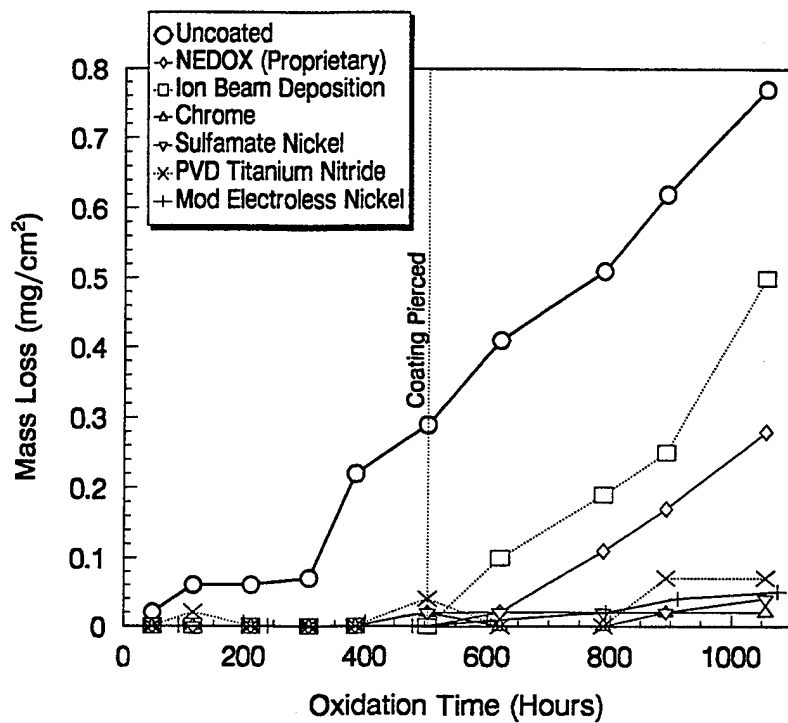
corrosion resistance. Each of the processes was tested for corrosion and wear resistance using ASTM D 4636 and the Cameron-Plint apparatus, respectively. A more complete description of the tests is provided in the following sections.

2. Oxidation-Corrosion Tests With Surface-Treated Specimens

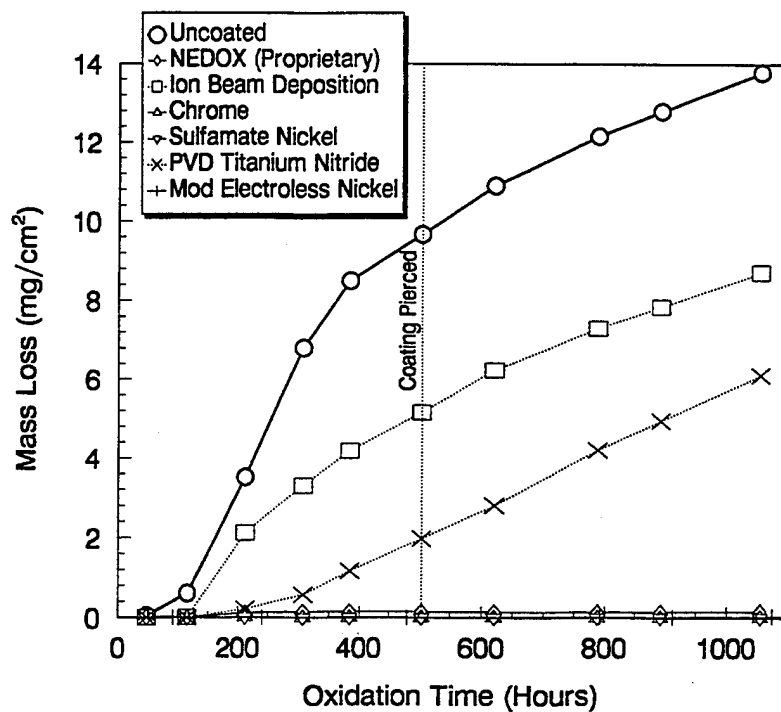
Oxidation-corrosion tests were performed with surface-treated C-93200 test coupons (Contact E in TABLE 2) immersed in CTFE fluid at 135 and 175°C. An untreated coupon was also tested as a baseline for comparison. No metallurgy or fluids other than C-93200 bronze and CTFE were evaluated. The acid number and viscosity of the CTFE fluid were not measured, as preceding test results detailed in Fig. 6 indicated that no change in these parameters was observed at these conditions. The remainder of the test procedure exactly duplicates the preceding results detailed in Section V-A.

The normalized material removal rate is plotted in Figs. 15a and 15b as a function of time at 135 and 175°C, respectively. Relatively severe corrosion is present on the untreated specimens at 175°C, and the results closely reflect those shown in Fig. 7. Material removal was significantly reduced by each of the surface coatings, although the IBD Chrome and PVD Titanium Nitride were only partially successful. Indeed, considerable flaking of both surface treatment processes was apparent and is denoted in Fig. 15 by the broken lines. Slight discoloration of the NEDOX coating was apparent. The remaining surface coatings (chrome, sulfamate nickel, and modified electroless nickel) remained completely untarnished and appear similar to the pretest finish.

The complete surface of each treated specimen was covered by the protective coating prior to the initiation of the oxidation-corrosion test. As a result, no corrosion of any coated specimen was observed during the first 500 hours of testing at 135°C. However, during practical applications, some penetration of the thin surface coating is likely to occur due to accidental scratching or wear. The effect of such damage was simulated by indenting the surface of each specimen through the protective coating at 500 hours, as denoted by the vertical broken line in Fig. 15.



a. 135°C



b. 175°C

(Note: The broken lines indicate that the surface coating has begun to flake from the surface.)

Figure 15. Mass loss from surface-treated C-93200 specimens immersed in CTFE hydraulic fluid

At high temperature (175°C), the material removal rate is not affected by the indentation, as in many instances severe corrosion was already present. At low temperatures, surface corrosion of the less well-adhered coatings was greatly increased by the localized penetration of the surface coating. The increased corrosion is apparent on the IBD Chrome and PVD Titanium Nitride. Slightly increased corrosion of the NEDOX specimen was also observed at low temperature. As previously stated, NEDOX was successful at high temperature but showed some discoloration at the conclusion of the test.

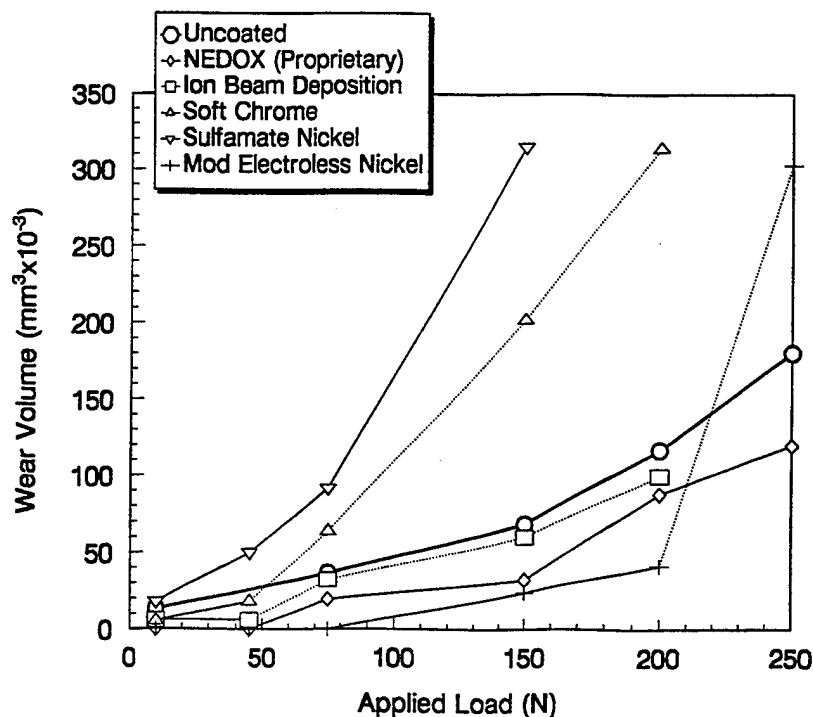
3. Wear Tests With Surface-Treated Specimens

Laboratory wear test procedures were performed using the Cameron-Plint wear test apparatus, according to the test conditions detailed in TABLE 8. During these tests, an AISI E 52100 steel ball slides on the surface-treated bronze specimens. The total wear volume was measured using a Talysurf profilometer. The wear test results are provided in Fig. 16 and represent the material removed from the coated bronze specimen. No wear was present on the opposing hard steel ball.

TABLE 8. Contact Parameters for Cameron-Plint Wear Tests With Surface-Treated C-93200 Bronze Lubricated With CTFE

| Parameter | Value |
|----------------------|-----------|
| Speed, Hz | 5 |
| Speed, mm/s | 47.6 |
| Load, N | 10 to 250 |
| Pressure, MPa | 35 to 141 |
| Temperature, °C | 125 |
| Duration, min | 30 |
| Amplitude, mm | 4.76 |
| Sliding distance, mm | 85,680 |

Relatively large variations in wear rate were observed on the coated specimen. Indeed, measured wear rate was apparently increased by application of both the soft chrome and sulfamate nickel surface treatments. The chrome coating does not adhere well to the bronze surface and is eliminated at loads above 50 N (as denoted by the broken line in Fig. 16) to leave a deeper wear



[Note: a) The broken lines indicate that the surface coating has been removed from the surface due to wear.
 b) The bronze specimens had a Root Mean Square (RMS) surface finish of 1.37 μm at a filter cutoff length of 0.8 mm.
 c) No wear tests were performed with PVD Titanium Nitride due to poor adhesion with bronze substrate.]

Figure 16. Wear test results obtained with surface-treated C-93200 bronze specimens

scar. In contrast, the sulfamate nickel coating showed good adhesion but had low hardness ($22 R_c$) combined with a high application thickness ($>10 \mu\text{m}$). As a result, deformation of the adhered sulfamate nickel layer gives apparently high wear, even at low applied loads. Similarly, the ion beam-deposited layer is removed at loads above 50 N but is sufficiently thin to make little difference in the perceived wear rate. However, the comparatively hard ion beam-deposited layer is effective at low loads prior to subsurface deformation and removal of the surface coating.

The hard NEDOX SF-2 and modified electroless nickel surface coatings, both of which consist of a nickel/polymer composite, appear to be the most effective overall surface treatment processes. Both coatings were previously shown to eliminate surface corrosion and may be seen to minimize wear in Fig. 16. No flaking or removal of the NEDOX coating was present even under the severe test conditions, while penetration of the modified electroless nickel coating only occurred in the most highly loaded tests.

VI. DISCUSSION

The primary objective of the present study was to define the suitability of a nonflammable chlorotrifluoroethylene (CTFE) hydraulic fluid for use in a gun recoil brake mechanism, using laboratory wear tests. During practical operation, a number of metallurgies are present, and disparate contact conditions are expected to occur. Indeed, the expected contact loads have not been precisely defined. Similarly, secondary effects, such as cavitation around the piston, could not be included. As a result, the program initially considered the range of metals likely to be present and a similarly broad range of contact variables. Previous workers have concluded that consideration of a wide range of contact parameters is required, even for the successful characterization of fluids intended for use in a well-defined system.⁽¹⁷⁾ The effects considered in this work include oil degradation, temperature, sliding speed, and applied load. Later tests focused on those parameters found to be most critical, i.e., the C-93200 bronze metallurgy, low sliding speeds, and relatively high temperatures. The study was organized in two distinct sections: artificial oil degradation (with chemical analysis) and wear testing. The performance of the CTFE fluid in each section was then compared with well-defined petroleum-, PAO-, and silicone-based oils.

Previous work has indicated relatively severe corrosion of bronze by unformulated CTFE at 175°C, which corresponds to the Advanced Field Artillery System (AFAS) operating envelope.^(6, 23) The results of the present study indicate that formulated CTFE fluid will corrode bronze and each of its elemental constituents (i.e., elementally pure copper, lead, tin, and zinc) at temperatures as low as 135°C. Operation at lower temperatures will greatly reduce the level of corrosion observed, as will use of appropriate surface treatment procedures. The level of degradation appears more severe than that observed in previous studies with alternate metallurgies.⁽⁶⁾ Chlorine and trace quantities of bromine in the hydraulic fluid seem to be the main cause of corrosion. Previous studies have also noted degradation of copper by CTFE, although little corrosion was present on either the copper or steel metallurgies used in the gun recoil mechanism in the present study.⁽⁶⁾ A number of surface treatment processes, which reduce or even eliminate corrosion of the bronze substrate, were identified. In addition, two of

the processes provide greatly improved wear resistance, due largely to increased surface hardness. No degradation of the CTFE fluid was evident using FTIR analysis.

It is recognized that the test severity necessary to achieve oil degradation in a practical time period necessitates use of a severe environment. For example, the laboratory tests were performed in an environment saturated with dry air which was shown to accelerate the degradation process, although the recoil brake mechanism will be a closed system. However, fluid temperatures of 121°C are common in currently used equipment, with temperatures of up to 177°C observed in some prototype testing.(23) Indeed, the test conditions were considerably less demanding than some previous studies performed at higher temperatures in the presence of moisture (6), with a corresponding reduction in test duration. To put this in perspective, both the petroleum- and PAO-based fluids eventually suffered severe degradation in the present laboratory study but normally provide acceptable field service.

In general, the oil degradation process of the hydrocarbon-based fluids is very different from that of CTFE, which showed no change in TAN, viscosity, or composition as defined by FTIR in Appendix D (although some degradation was apparent using GC). Moreover, a distinct initiation period was present prior to the breakpoint of the hydrocarbon-based fluids, while chemical corrosion of the bronze material occurred immediately after commencing the test with CTFE. As a result, no direct comparison may be made between the high temperature stability of the CTFE and hydrocarbon-based oils, although the results of the present study indicate that corrosion of bronze and a number of other elements by CTFE fluid would commence immediately on initiation of high temperature operation above approximately 135°C. The effect of chemical reaction between CTFE and bronze in practical application of the gun recoil brake mechanism is unclear and will depend to a great extent on the operating environment. Previously, however, full-scale pump loop tests have indicated surface corrosion with a similar but possibly not identical fluid.(7)

Lubricant decomposition components can be either beneficial or detrimental to wear protection. Simultaneous corrosion and mild mechanical contact may result in a combined effect that is greater than the additive effect of each process taken alone, although formation of an effective

chemical film is necessary to reduce adhesive wear and scuffing.(11) The wear tests performed in this study indicate that the previously described surface corrosion does indeed affect the observed wear mechanism. In general, however, the laboratory wear tests performed using both the Cameron-Plint and four-ball apparatus indicate that the lubricity of the CTFE fluid was similar to that of the hydrocarbon-based oils and appreciably better than that of the silicone fluid. In no instance was the lubricity of the CTFE oils less than that of the MIL-H-6083 baseline fluid, which has given excellent field service for many years.(3, 7) In addition, the poor viscosity index of the CTFE fluids will reduce hydrodynamic lift during laboratory testing compared with the PAO- and silicone-based oils, both of which have excellent viscosity retention at higher temperatures.(11)

During consideration of the results, it should be noted that the lubricating qualities of polydimethylsiloxanes or silicone fluids are typically poor.(11, 24) This result is partially due to the low pressure-viscosity coefficient of silicone causing inferior elastohydrodynamic film formation (distinct from hydrodynamic). In addition, dimethylsilicones do not normally form boundary films in a manner similar to hydrocarbon surfactants, such as fatty acids, although weak films have been reported at higher temperatures.(22) Finally, the boundary lubricating characteristics of the silicone fluids may not normally be greatly improved using additives, which seriously restricts their use in systems in which hydrodynamic or full-fluid lubrication is likely to fail.(24)

A secondary objective was to compare the relative performance of a typical PAO-based fluid qualified under MIL-H-46170 and a lower viscosity single hydraulic fluid intended for use in low temperature conditions, referred to as SHF in the present report. The results indicate that both fluids have good boundary lubricating characteristics. In general, the tests indicated marginally increased wear with the low viscosity single hydraulic fluid, probably due to decreased hydrodynamic and elastohydrodynamic lift. Similarly, the low viscosity oil had reduced high-temperature stability. However, both of these effects are likely to be eliminated in the intended operating environment for the low viscosity oil.

During the present study, the normalized wear coefficient for the hydrocarbon and CTFE fluid ranged between 0.05 and 2.0×10^{-6} , which typically corresponds to a lubricant of average quality in a contact of dissimilar metals⁷.⁽²¹⁾ However, in general, the most that may be expected from any practical laboratory wear test procedure is an accurate qualitative ranking in comparison to other fluids of known quality.⁽¹⁷⁾ Overall, the results indicate that the PAO-based oil provides marginally the best boundary wear protection for the fluids and conditions considered. Nonetheless, the CTFE fluid should provide good wear protection under boundary-lubricated conditions at all but the highest operating temperatures. Higher temperatures will promote surface corrosion in bronze alloys, which may be augmented by sliding wear. However, the temperature required to produce corrosion with CTFE would **eventually** also cause severe degradation of the petroleum and PAO fluids.

VII. CONCLUSIONS

The following conclusions may be drawn from the laboratory tests performed during the course of the study:

- a. The level of wear observed at normal operating temperatures with CTFE oil qualified under MIL-H-53119 was comparable to petroleum-based fluids qualified under MIL-H-6083 and so should be acceptable in practical applications.
- b. The PAO-based oil qualified under MIL-H-46170 normally provided marginally better wear protection than both the petroleum- and CTFE-based fluids.
- c. Severe friction and wear were present for the silicone-based fluids in the absence of hydrodynamic lift.

⁷ Considerable disagreement exists in the literature with regard to the value of Archard's wear coefficient that corresponds to acceptable lubrication.^(19, 25-27)

- d. The single (low viscosity) hydraulic fluid (i.e., SHF) produced marginally higher wear than MIL-H-46170 but should be acceptable in a cold operating environment.
- e. The single (low viscosity) hydraulic fluid (i.e., SHF) had slightly lower thermal stability than MIL-H-46170 but should be acceptable in a cold operating environment.
- f. CTFE produced severe corrosion of bronze and elementally pure copper, lead, tin, and zinc at temperatures above approximately 135°C. The rate of material removal increased disproportionately at temperatures above this value. Corrosion begins immediately following immersion in the fluid.
- g. CTFE fluid provides good lubricating qualities and corrosion resistance with ferrous metallurgies.
- h. No change in either acid number or viscosity was observed for the CTFE fluid during oxidation-corrosion tests in the absence of moisture at temperatures up to 175°C.
- i. Corrosion of bronze by CTFE may be due to preferential reaction with near-surface material by chlorine and trace quantities of bromine.
- j. Increased acid number and viscosity were observed for the formulated hydrocarbon fluids during high temperature oxidation-corrosion tests after an appreciable initiation period. However, metallic corrosion was comparatively mild compared to the CTFE-based oil.
- k. Of the fluids studied, MIL-B-46176, derived from a silicone basestock, provided optimum thermal stability.
- l. The basestock for the CTFE fluid showed very similar stability and wear characteristics compared to the formulated fluid.

- m. The basestocks for the petroleum and PAO fluids had inferior stability and wear characteristics compared to the formulated fluid.
- n. Both surface corrosion and wear of bronze lubricated with CTFE may be greatly reduced through use of NEDOX SF-2 or Wear Cote CF_x surface treatment processes.
- o. Corrosion of bronze by CTFE is greatly reduced in an oxygen-free environment.

VIII. RECOMMENDATIONS FOR FURTHER STUDY

The following items are recommended for further study:

1. Define the normal and worst-case operating conditions within the gun recoil brake mechanism, with particular reference to temperature.
2. Define the wear mechanisms present with bronze specimens using more detailed surface chemical analysis, with particular reference to applied load and temperature.
3. Define the corrosion mechanisms present in the CTFE fluid during high temperature oxidation-corrosion tests using more detailed chemical analysis. Perform additional corrosion tests using CTFE that is free of bromine.
4. Define the combined effects of surface corrosion and mechanical wear with CTFE under extended operation at very low load conditions.
5. Define the combined effects of CTFE and various surface treatment processes on the wear rate associated with various lip seals used in the gun recoil mechanism.

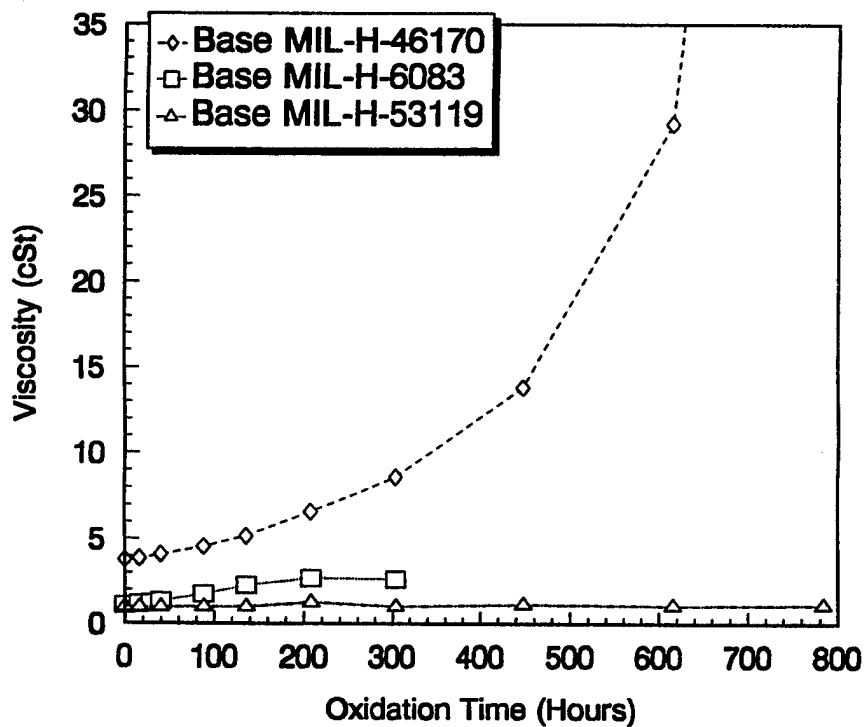
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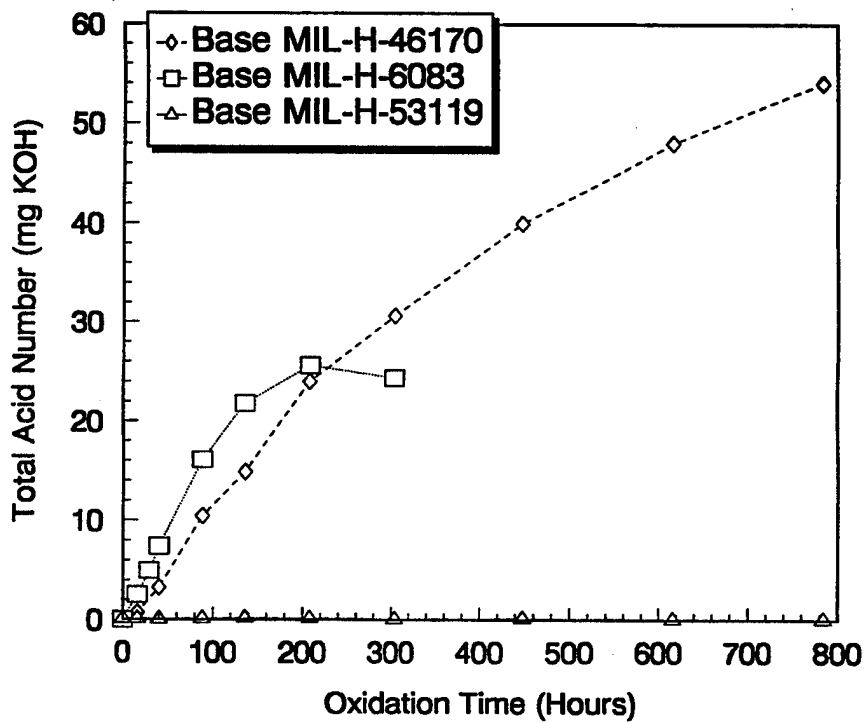
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APPENDIX A

Mass Loss Due to Corrosion During Oxidation Tests

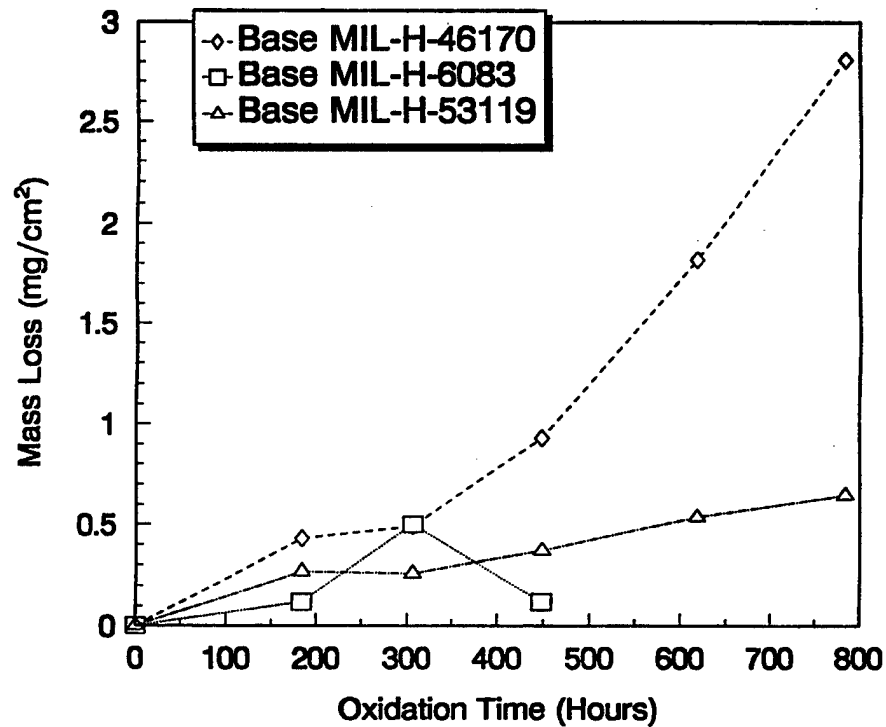


a. Kinematic viscosity at 100°C

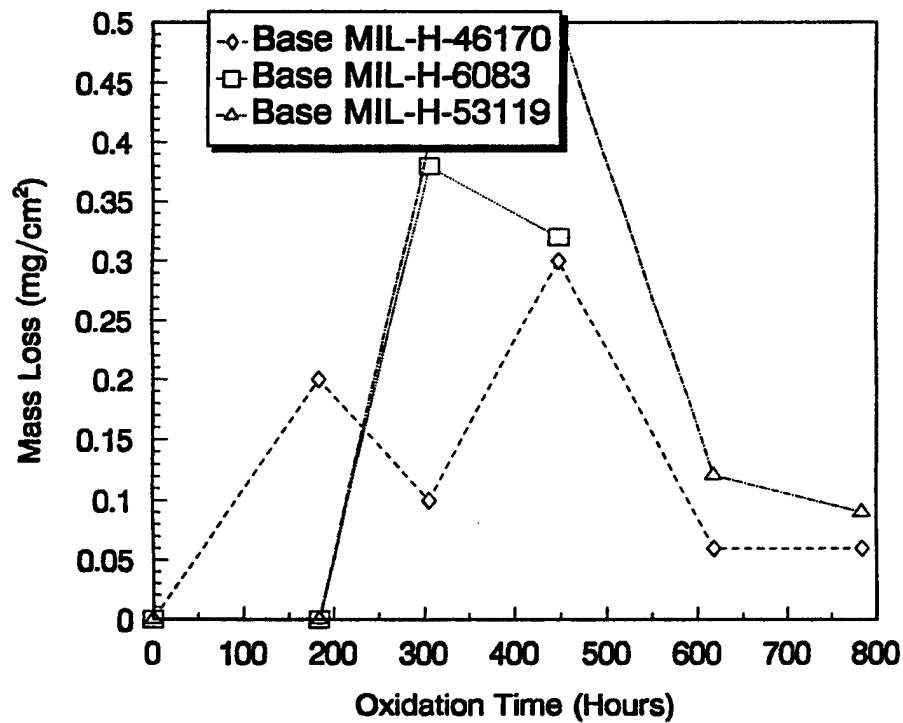


b. Total Acid Number

Figure A-1. Oil degradation measured during oxidation-corrosion tests with unformulated oil performed according to ASTM D 4636 at 135°C

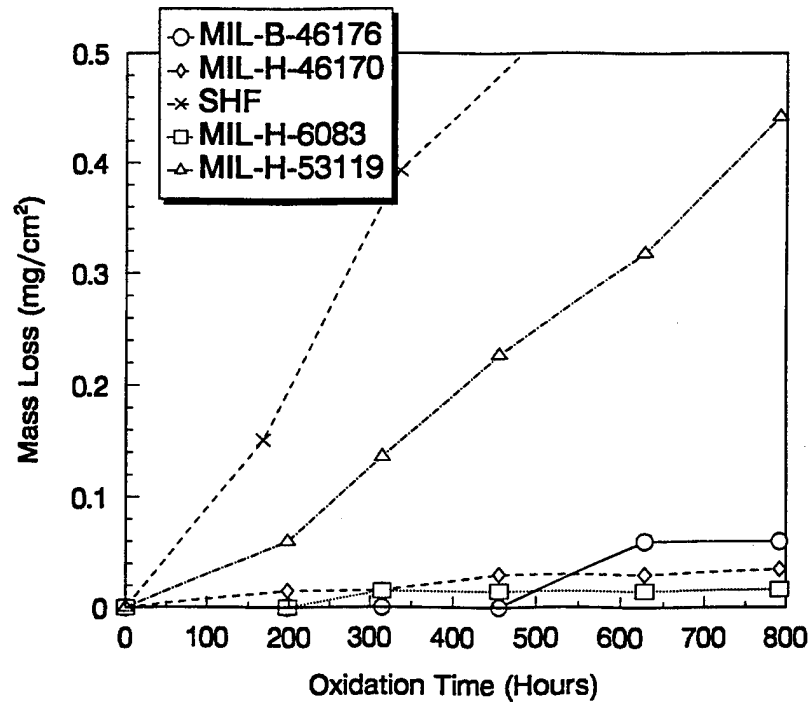


a. C-93200 high-lead tin bronze

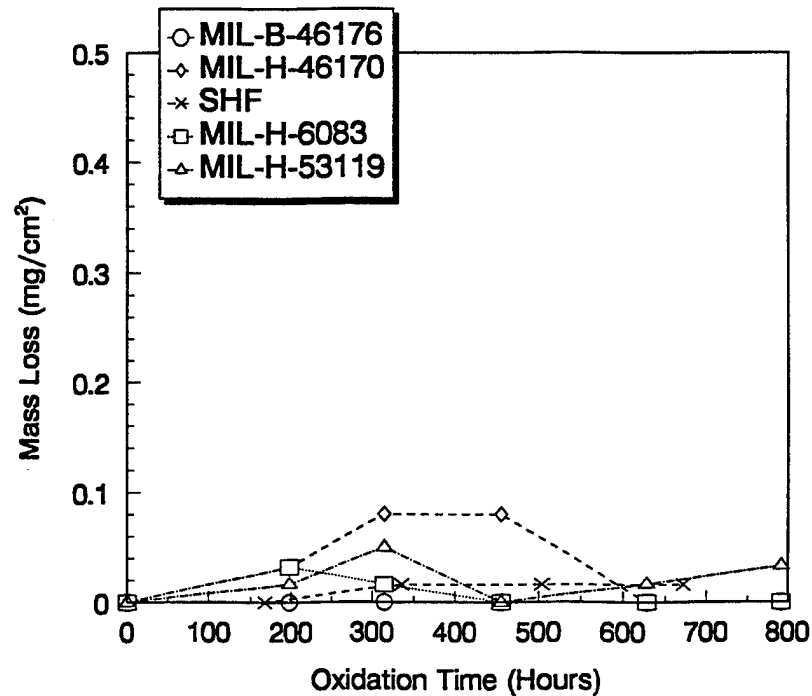


b. Copper alloy NR 955

Figure A-2. Mass loss measured on different metallurgies during oxidation tests at 135°C with basestock fluids



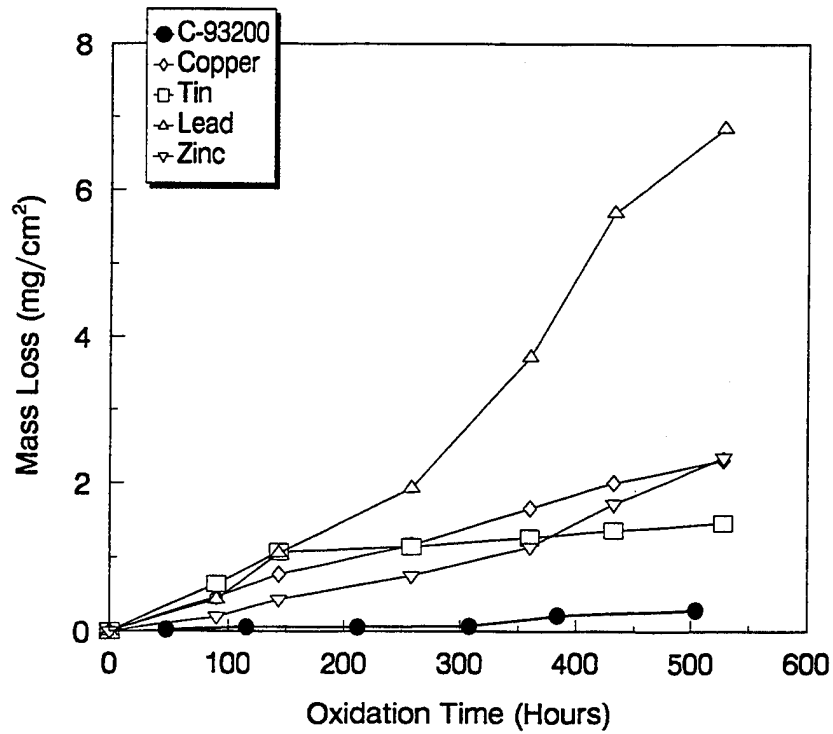
a. Copper alloy NR 955



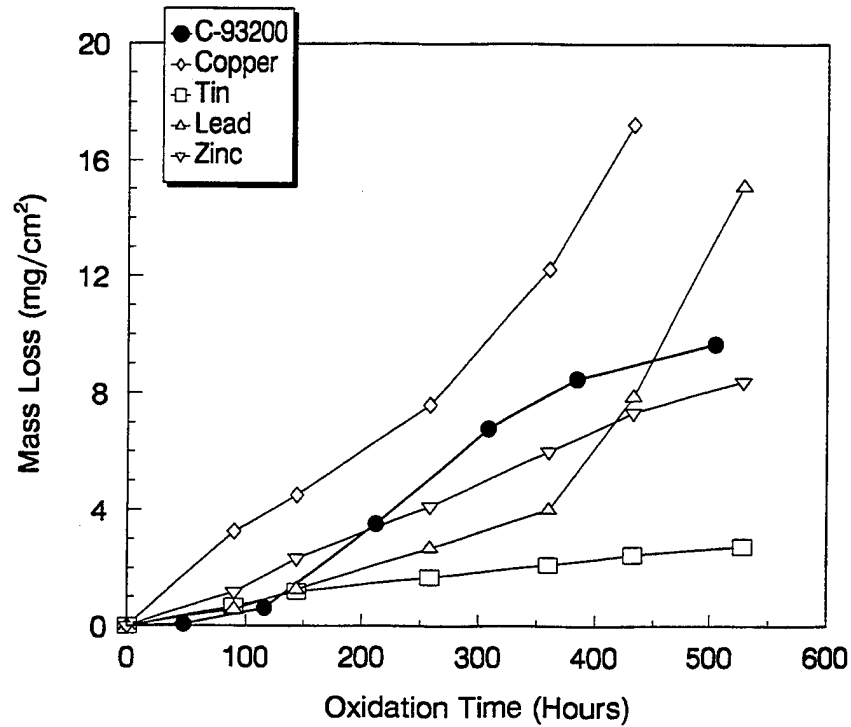
b. 4140 steel

(Note: The results for C-93200 are provided in Fig. 7 in the main body of the text.)

Figure A-3. Mass loss measured on different metallurgies from the gun recoil mechanism during oxidation-corrosion tests with fully formulated fluids at 175°C



a. 135°C



b. 175°C

Figure A-4. Mass loss from elemental constituents of C-93200 bronze during oxidation-corrosion tests performed according to ASTM D 4636 performed using CTFE

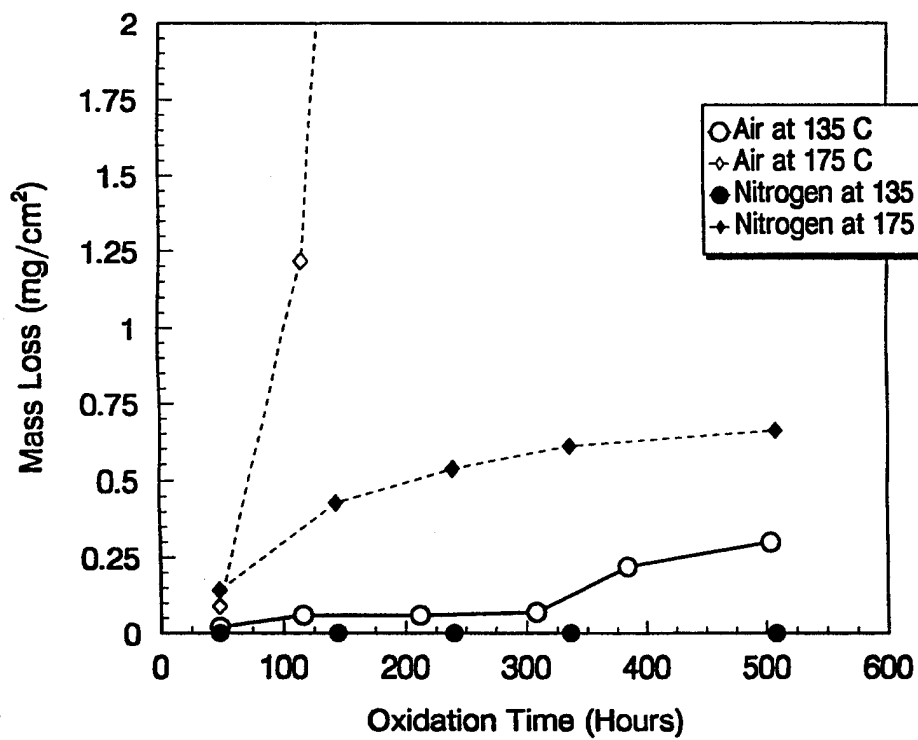
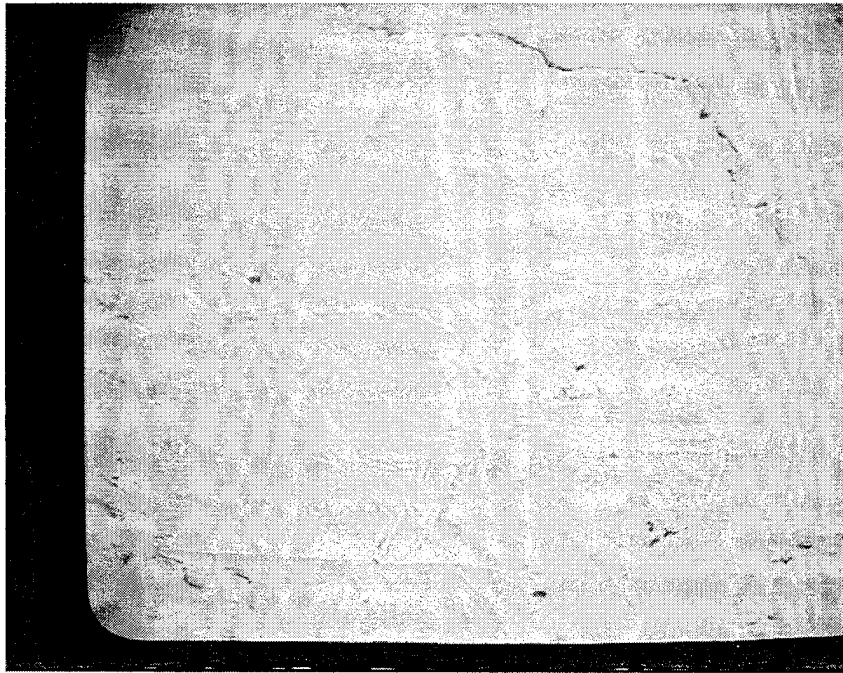
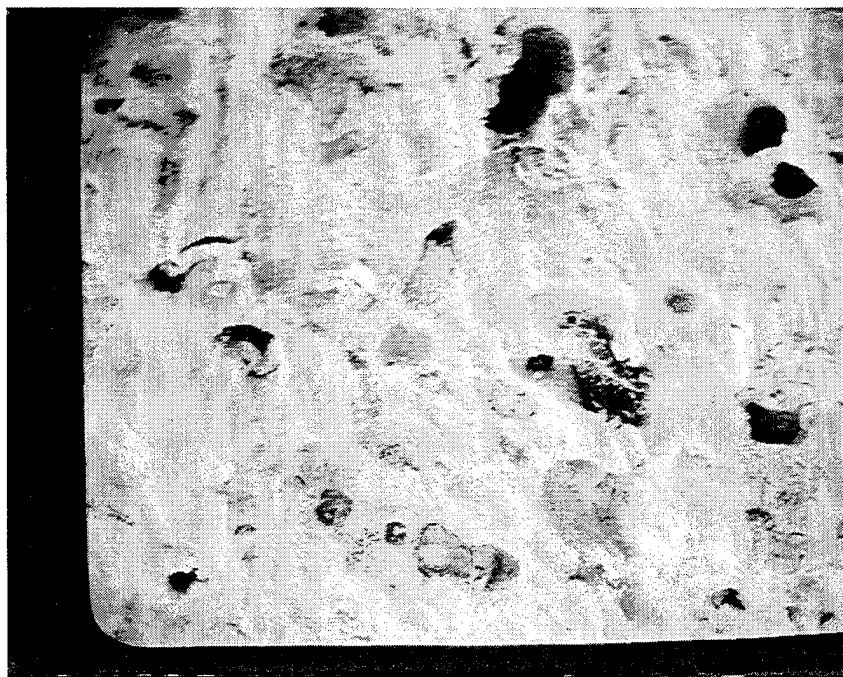


Figure A-5. Comparison of surface corrosion of C-93200 by CTFE in air and nitrogen

APPENDIX B
SEM Micrographs



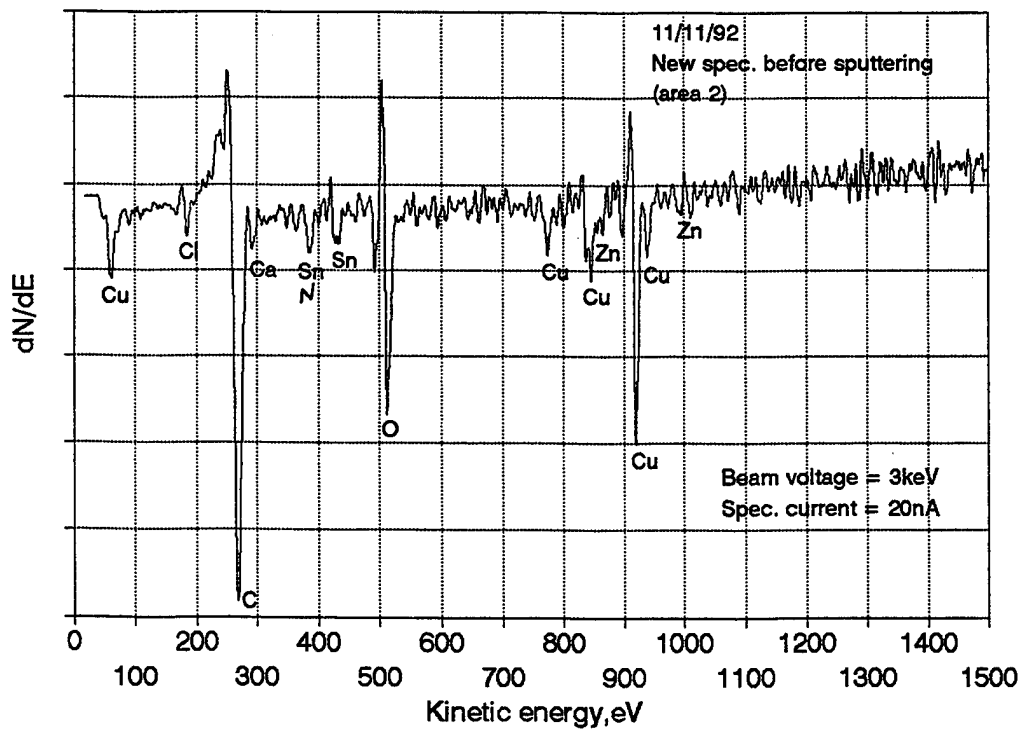
a. New specimen



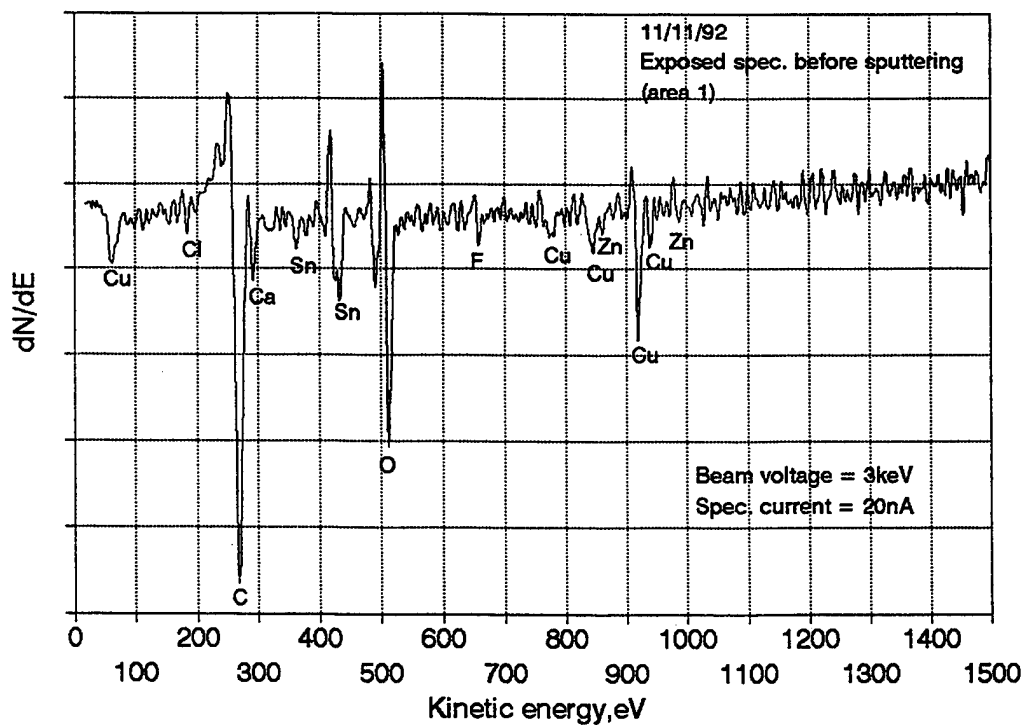
b. Specimen immersed in CTFE at 175°C for 800 hours

Figure B-1. Scanning electron micrographs of C-93200 surface topography

APPENDIX C
Results of AES Analysis

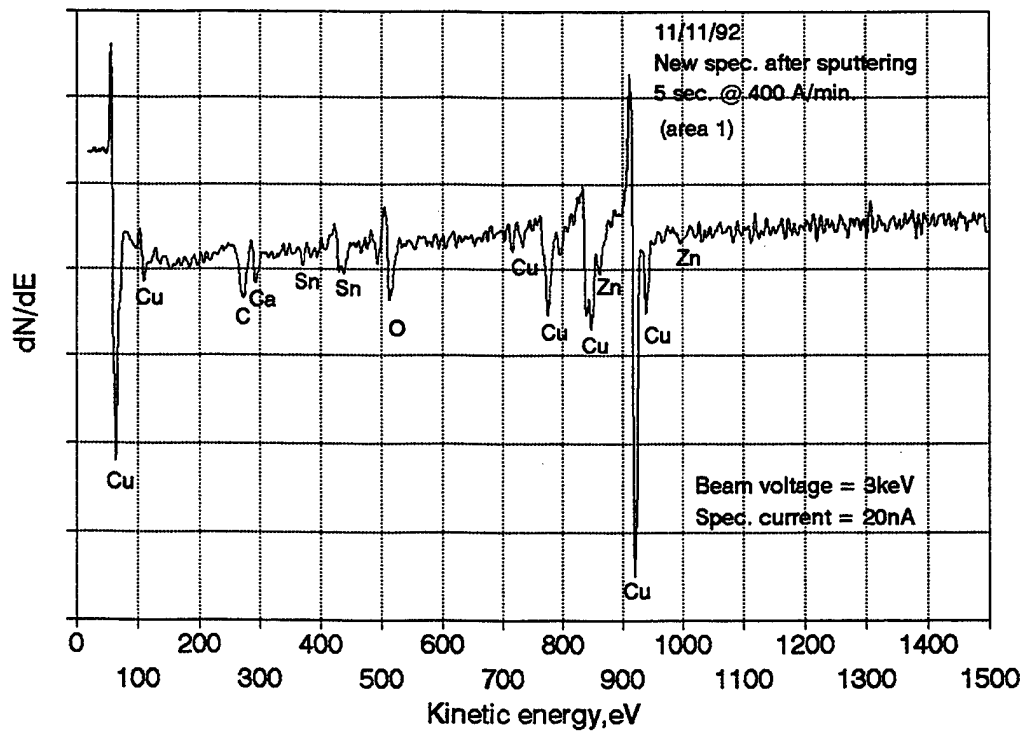


a. New specimen

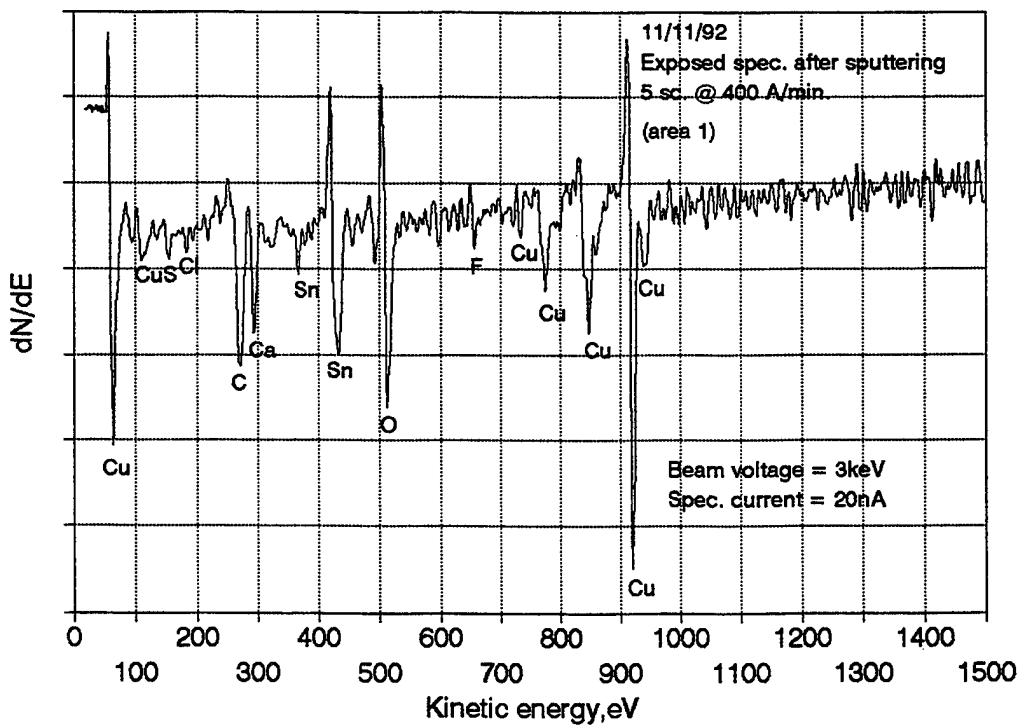


b. Corroded specimen

Figure C-1. Results of AES analysis on C-93200 bronze

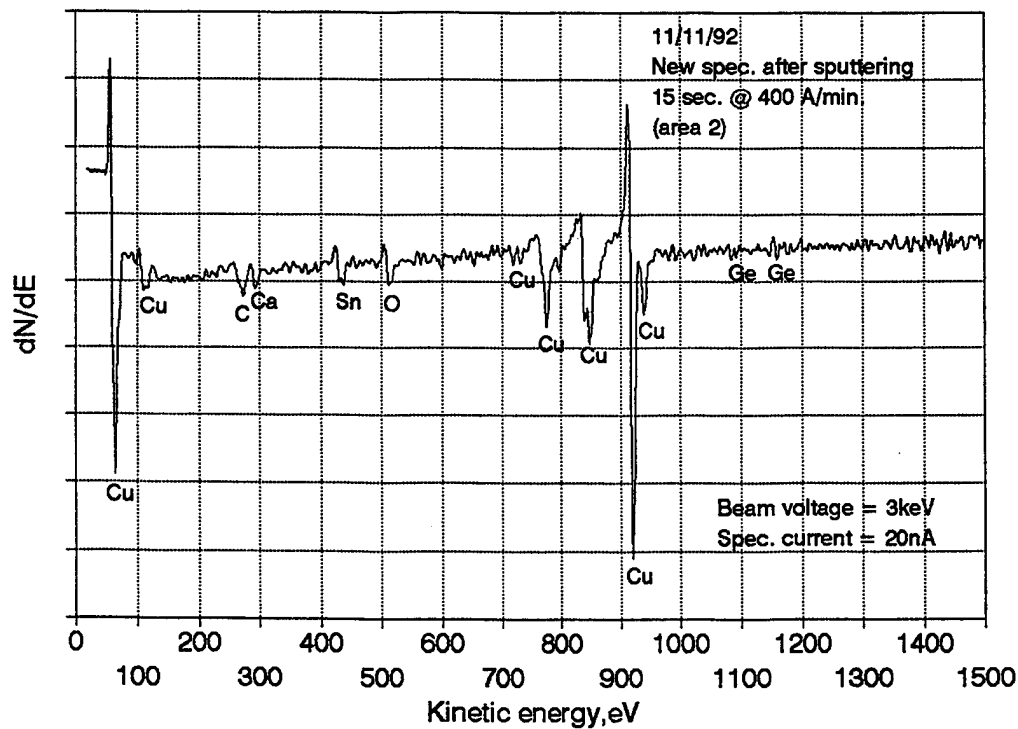


a. New specimen

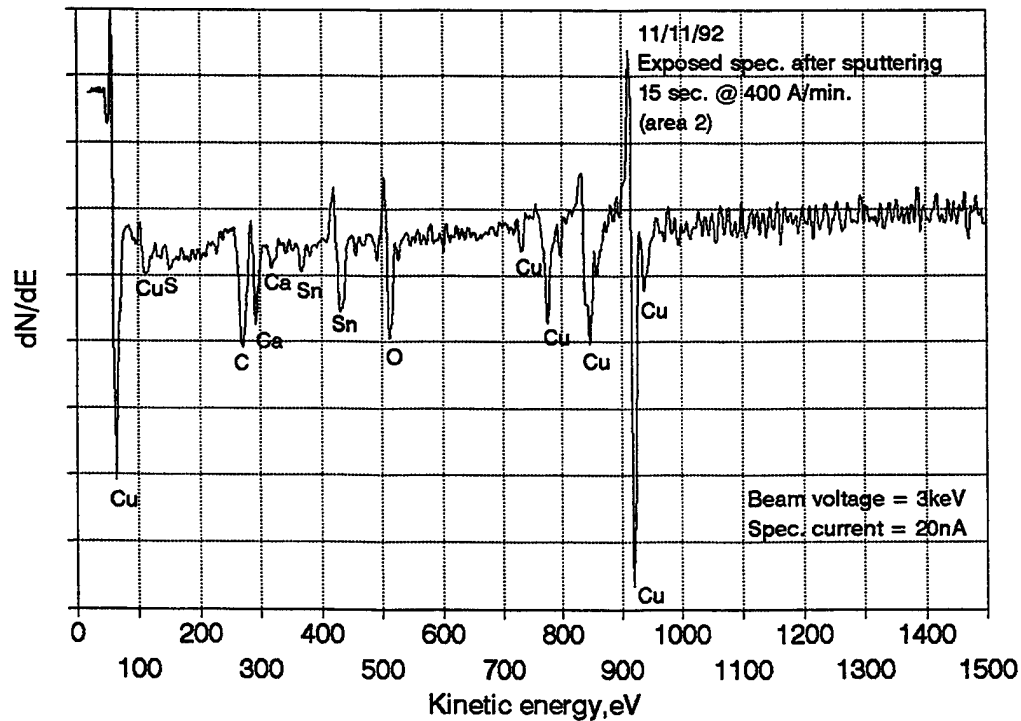


b. Corroded specimen

Figure C-2. Results of AES analysis on C-93200 sputtered to a depth of approximately 33 angstroms



a. New specimen



b. Corroded specimen

Figure C-3. Results of AES analysis on C-93200 sputtered to a depth of approximately 100 angstroms

APPENDIX D
Data From FTIR Analysis

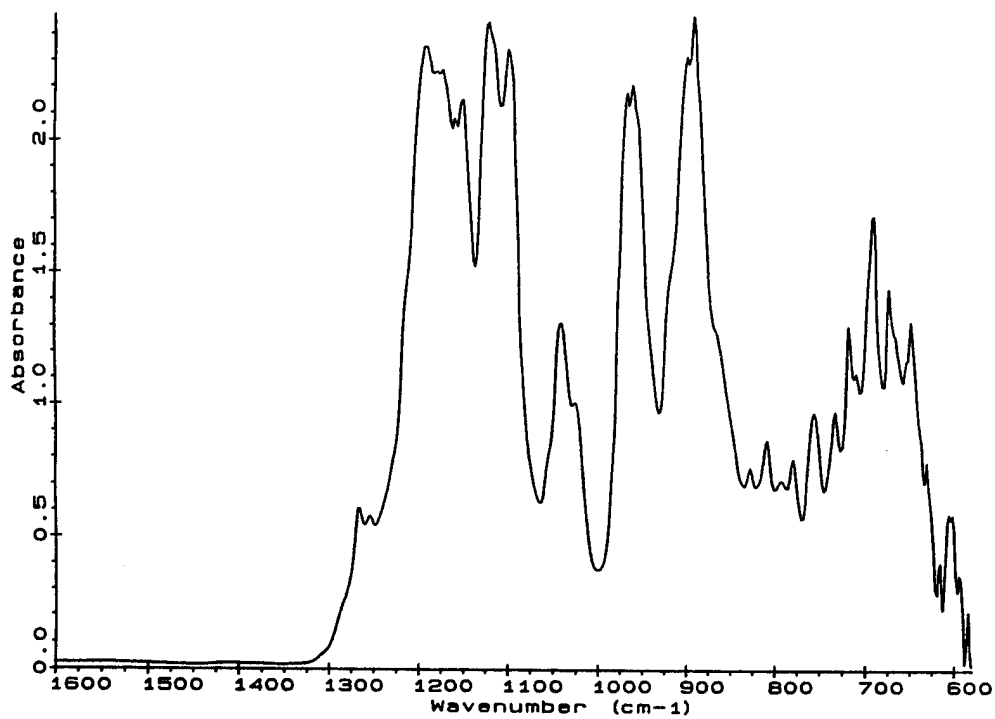


Figure D-1. FTIR spectrum for unused (formulated) CTFE fluid

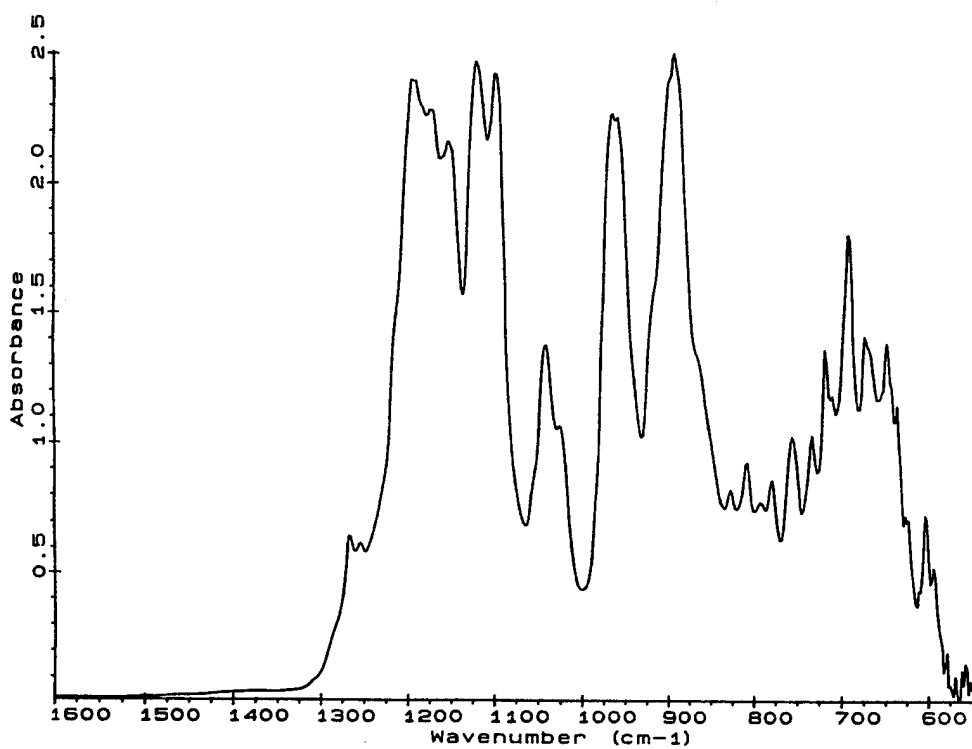


Figure D-2. FTIR spectrum for basestock (unformulated) CTFE fluid

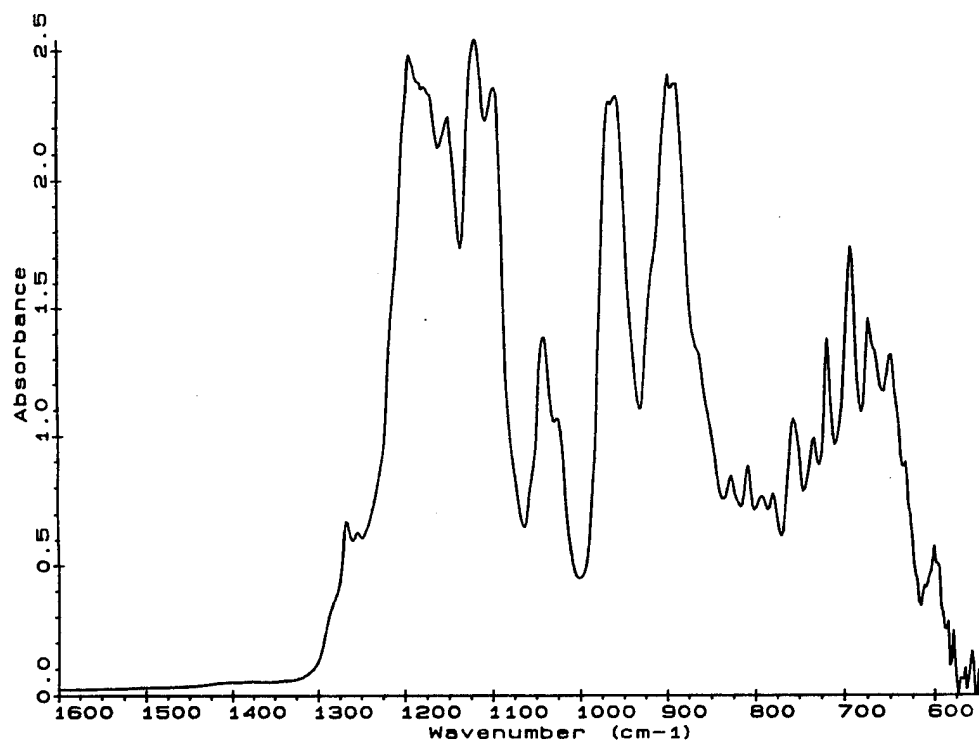


Figure D-3. FTIR spectrum for stressed CTFE fluid

APPENDIX E

Description of Dow Corning Silicone Fluid

Information About Dow Corning Silicone Fluids

DOW CORNING

DESCRIPTION

200® fluids, 50-1000 centistokes (cs), are medium viscosity polydimethylsiloxane polymers manufactured to yield essentially linear polymers with average kinematic viscosities ranging from 50 to 1000 cs.

COMPOSITION

Linear polydimethylsiloxane polymers characteristically have the following typical chemical composition:



Commercial bulk-polymerized dimethyl silicone fluids, such as 200 fluids, 50-1000 cs, typically contain trace amounts of process impurities.

BENEFITS

200 fluids, 50-1000 cs, have the following product characteristics:

- Clear
- Essentially nontoxic
- Nonbioaccumulating
- Nonbioactive
- Nongreasy
- Nonocclusive
- Nonrancidifying
- Nonstinging on skin
- Tasteless

200 fluids, 50-1000 cs, when compared with other materials that may be substituted in a given application, may offer one or more of these comparative characteristics:

- High compressibility
- High damping action
- High dielectric strength
- High oxidation resistance*
- High shearability without breakdown
- High spreadability
- High temperature serviceability*
- High compatibility

200® Fluid, 50 cs
200® Fluid, 100 cs
200® Fluid, 200 cs
200® Fluid, 350 cs
200® Fluid, 500 cs
200® Fluid, 1000 cs

- High water repellency
- Low environmental hazard
- Low fire hazard*
- Low odor
- Low reactivity*
- Low surface energy
- Low temperature serviceability
- Low toxicity
- Low vapor pressure
- Good heat stability*
- Good leveling and easy rubout
- Soft feel and lubricity on skin

USES

200 fluids, 50-1000 cs, are not intended for food or medical use. They are intended for use by industrial manufacturers. Typical end uses include:

- Cosmetic ingredient
- Elastomer and plastics lubricant
- Electrical insulating fluid
- Foam preventative or breaker
- Household product ingredient
- Mechanical fluid
- Mold release agent
- Personal care product ingredient
- Polish ingredient

- Specialty chemical product ingredient
- Specialty cleaner ingredient
- Surface active agent

HOW TO USE

Since the applications for these fluids are numerous and varied, application methods and recommended concentration levels must be considered on an individual basis. Contact Dow Corning Product Information for specifics.

SHIPPING LIMITATIONS

None.

STORAGE AND SHELF LIFE

Shelf life is the period of time during which a material may be stored under specified conditions in its original unopened container (except for inspection) while retaining the material's sales specifications. Shelf life starts with the date of shipment (unless otherwise specified), and ends on a given date. Continued storage beyond

the designated shelf life does not necessarily mean that the material may not be used. However, after the expiration of the designated shelf life, testing of critical properties and redetermination of suitability for contemplated use of the product are imperative.

Dow Corning certifies that 200 fluids, 50-1000 cs, will meet sales specification requirements for a period of 12 months from date of shipment. Store in ambient temperatures.

PACKAGING

200 fluids, 50-1000 cs, are supplied in 40- and 440-lb (18.1- and 199.6-kg) containers, net weight. Smaller containers are available from repackagers.

Caution: Containers will have product residues when emptied. Follow precautions recommended for handling these products when disposing of the container. Containers are not intended for reuse.

INCOMING INSPECTION

Dow Corning recommends that incoming inspection tests be performed to confirm product identity and condition on arrival. Suggested tests include viscosity and infrared identification, and any other tests deemed necessary for the application. Such tests may or may not be run routinely by Dow Corning as lot acceptance tests. Obtain the sales specifications for lot acceptance tests and test limits conducted on 200 fluids, 50-1000 cs.

SALES SPECIFICATIONS

Sales specifications information, including detailed test methods and analysis procedures used by

Dow Corning, is available upon request. Since Dow Corning reserves the right to update sales specifications information without prior notice, users should periodically request this information.

SAFE HANDLING INFORMATION

200 fluids, 50-1000 cs, may cause temporary eye discomfort.

A Materials Safety Data Sheet, as required under existing federal regulations, is available upon request from Dow Corning Corporation, Midland, Michigan 48686-0994.

Note: For answers to any questions regarding the efficacy, safety, health or environmental aspects of using 200 fluids, 50-1000 cs, in any application, contact your nearest Dow Corning sales office or call Dow Corning Customer Service:
Outside Michigan (800) 248-2345

CONTAMINATION AND FIRE PREVENTION

At elevated temperatures, 200 fluids, 50-1000 cs, are sensitive to contamination by strong acids, bases, some metallic compounds and oxidizing agents. These contaminants may cause an accelerated rate of volatile by-product formation. Oxidizing agents can also cause an increase in fluid viscosity. When these conditions may exist, it is recommended that the flash point of the fluids be checked periodically to monitor operational safety. Also, ignitable conditions may exist if the fluid is giving off smoke.

MSDS INFORMATION

ATTENTION: PRODUCT SAFETY INFORMATION REQUIRED FOR

SAFE USE IS NOT INCLUDED. BEFORE HANDLING, READ PRODUCT AND MATERIAL SAFETY DATA SHEETS AND CONTAINER LABELS FOR SAFE USE, PHYSICAL AND HEALTH HAZARD INFORMATION. THE MATERIAL SAFETY DATA SHEET IS AVAILABLE FROM YOUR DOW CORNING REPRESENTATIVE, OR DISTRIBUTOR, OR BY WRITING TO DOW CORNING CUSTOMER SERVICE, OR BY CALLING (517) 496-6000.

WARRANTY INFORMATION - PLEASE READ CAREFULLY

Dow Corning believes that the information in this publication is an accurate description of the typical characteristics and/or uses of the product or products, but it is your responsibility to thoroughly test the product in your specific application to determine its performance, efficacy and safety.

Unless Dow Corning provides you with a specific written warranty of fitness for a particular use, Dow Corning's sole warranty is that the product or products will meet Dow Corning's then current sales specifications.

DOW CORNING SPECIFICALLY DISCLAIMS ANY OTHER EXPRESS OR IMPLIED WARRANTY, INCLUDING THE WARRANTIES OF MERCHANTABILITY AND OF FITNESS FOR USE. Your exclusive remedy and Dow Corning's sole liability for breach of warranty is limited to refund of the purchase price or replacement of any product shown to be other than as warranted, and Dow Corning expressly disclaims any liability for incidental or consequential damages.

TYPICAL PROPERTIES

These values are not intended for use in preparing specifications¹.

| <i>As supplied</i> | <i>200 Fluid, 50 cs</i> | <i>200 Fluid, 100 cs</i> | <i>200 Fluid, 200 cs</i> | <i>200 Fluid, 350 cs</i> | <i>200 Fluid, 500 cs</i> | <i>200 Fluid, 1000 cs</i> |
|---|--|------------------------------|------------------------------|------------------------------|------------------------------|-------------------------------|
| Appearance | Crystal clear liquid from suspended matter and sediment. | | | | | |
| Specific Gravity at 25 C (77 F) | 0.960 | 0.964 | 0.967 | 0.968 | 0.969 | 0.970 |
| Refractive Index at 25 C (77 F) | 1.4022 | 1.4030 | 1.4032 | 1.4034 | 1.4034 | 1.4035 |
| Color, APHA | 5 | 5 | 5 | 5 | 5 | 5 |
| Flash Point, open cup, °C (°F) | 318 (605) | >326 (>620) | >326 (>620) | >326 (>620) | >326 (>620) | >326 (>620) |
| Acid Number, BCP | trace | trace | trace | trace | trace | trace |
| Melt Point, °C (°F) ^{2,3} | -41 (-42) | -28 (-18) | -27 (-17) | -26 (-15) | -26 (-15) | -25 (-13) |
| Pour Point, °C (°F) | -70 (-94) | -65 (-85) | -65 (-85) | -65 (-85) | -50 (-58) | -50 (-58) |
| Surface Tension at 25 C (77 F), dynes/cm | 20.8 | 20.9 | 21.0 | 21.1 | 21.1 | 21.2 |
| Volatile Content, at 150 C (302 F), percent | 0.3 | 0.02 | 0.07 | 0.09 | 0.15 | 0.11 |
| Viscosity Temperature Coefficient | 0.59 | 0.60 | 0.60 | 0.60 | 0.60 | 0.61 |
| Coefficient of Expansion, cc/cc/°C | 0.00104 | 0.00096 | 0.00096 | 0.00096 | 0.00096 | 0.00096 |
| Thermal Conductivity at 50 C (122 F), g cal/cm · sec · °C | - | 0.00037 | - | 0.00038 | - | 0.00038 |
| Specific Heat at 25 C (77 F), cal/g/cm | - | 0.352 | - | 0.350 | - | 0.349 |
| Solubility Parameter ⁴ | 7.3 | 7.4 | 7.4 | 7.4 | 7.4 | 7.4 |
| Solubility in Typical Solvents, | | | | | | |
| Chlorinated solvents | High | High | High | High | High | High |
| Aromatic solvents | High | High | High | High | High | High |
| Aliphatic solvents | High | High | High | High | High | High |
| Dry Alcohols | Poor | Poor | Poor | Poor | Poor | Poor |
| Water | Poor | Poor | Poor | Poor | Poor | Poor |
| Fluorinated propellents | High | High | High | High | High | High |
| Dielectric Strength at 25 C (77 F), volts/mil | 400 | 400 | 400 | 400 | 400 | 400 |
| Volume Resistivity at 25 C (77 F), ohm-cm | 1.0 x 10 ¹⁵ | 1.0 x 10 ¹⁵ | 1.0 x 10 ¹⁵ | 1.0 x 10 ¹⁵ | 1.0 x 10 ¹⁵ | 1.0 x 10 ¹⁵ |

¹Dow Corning does not routinely test all these physical properties. Users should independently test these properties when they are critical in the application.

²The melt point temperature is a typical value and may vary somewhat due to molecular distribution (especially 50 cs or less). If the melting point is critical to your application then several lots should be thoroughly evaluated.

³Due to different rates of cooling, this test method may yield pour points lower than the temperature at which these fluids would melt.

⁴Fedors Method: R.F. Fedors, Polymer Engineering and Science, Feb. 1974.

Specification Writers: Please contact Dow Corning Corporation, Midland, Michigan, before writing specifications on this product.

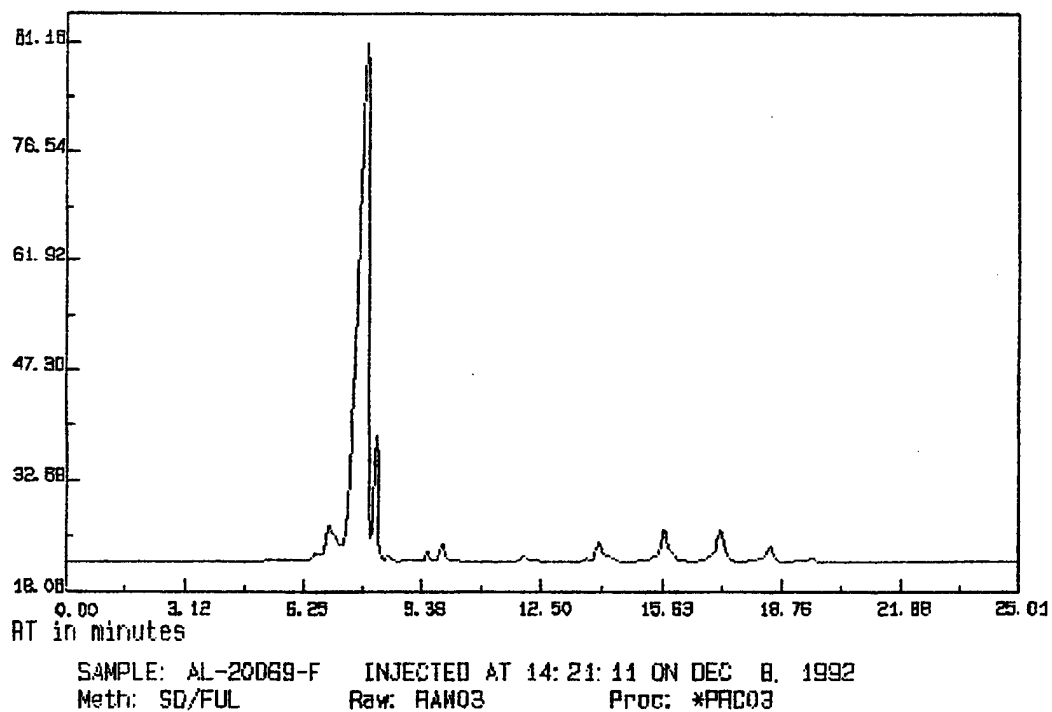
APPENDIX F

GC Analysis

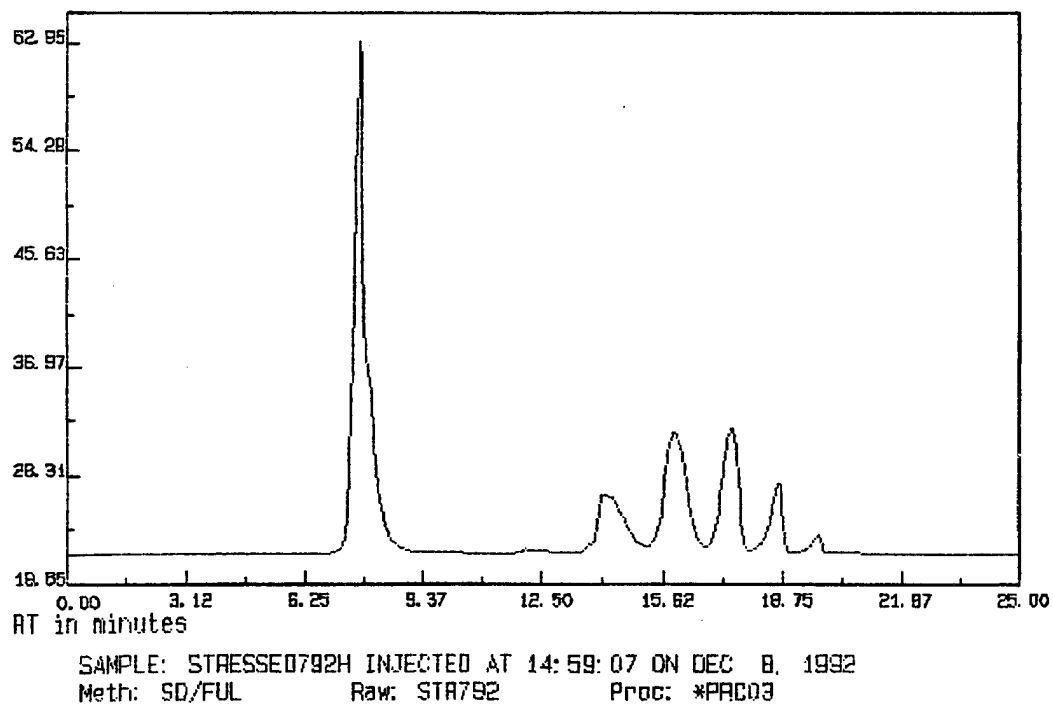
Gas chromatographic (GC) analysis was performed on the new CTFE fluid, as well as a sample oxidized at 175°C for 790 hours, with the results shown in Figs. F-1a and F-1b. The specific GC conditions used are given in TABLE F-1. Clearly, the fluid is a mixture of several components. Attempts to identify the components using GC coupled with mass spectroscopy were unsuccessful. However, qualitative examination of the spectra would indicate that this fluid is distinct from that used in some preceding studies, probably due to batch-to-batch variation in oligomer distribution.(6)

TABLE F-1. Gas Chromatographic Conditions

| | |
|-----------------------|---|
| Detector: | FID |
| Column: | 3 percent OV-101 Chromosorb W-HP 80/100 mesh |
| Length: | 6 ft |
| Diameter: | 0.125 in. |
| Carrier Gas: | 15 mL/min He |
| Detector Temperature: | 400°C |
| Column Temperature: | 20 to 390°C |
| Program Rate: | 8°C/min |
| Injection: | On column |
| Final Hold: | 5 min |
| Sample Size: | 1 µL |



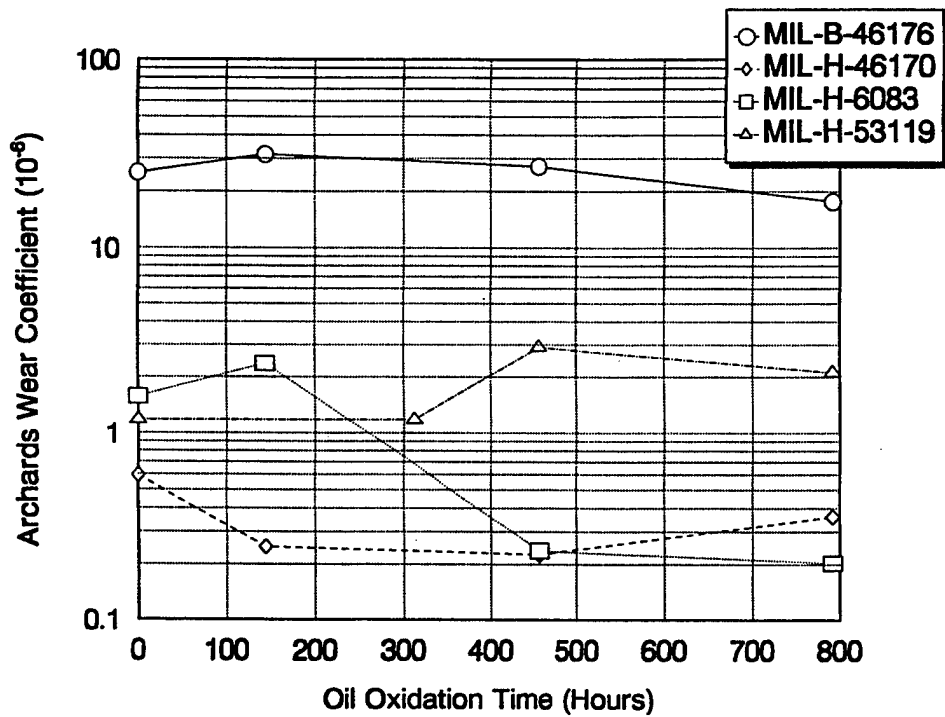
a. New and unused fluid



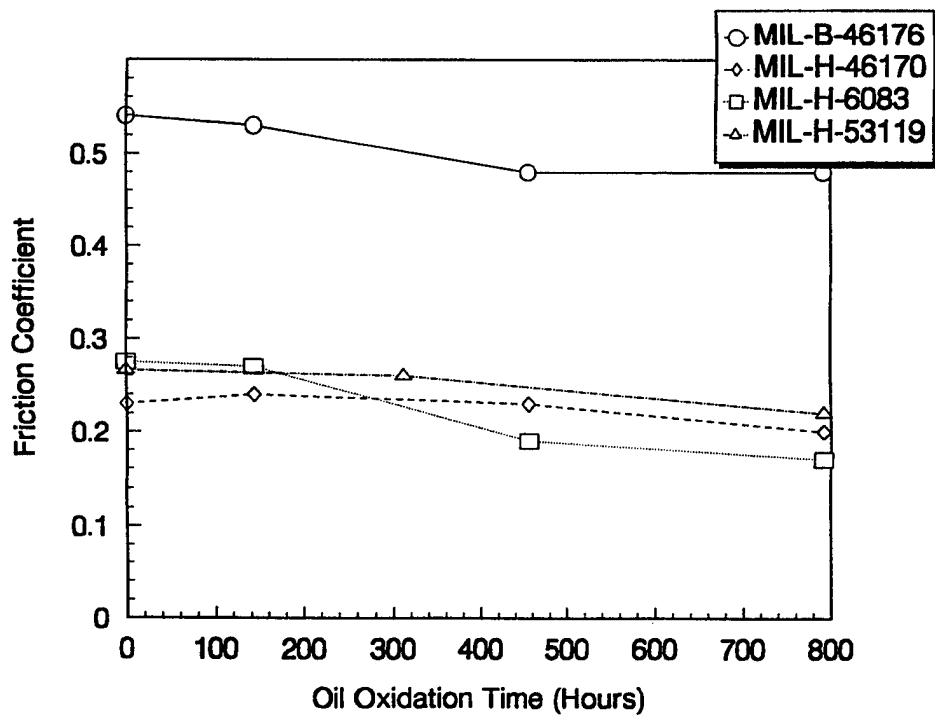
b. Oxidized oil

Figure F-1. Gas chromatograms for CTFE fluids

APPENDIX G
Effect of Oil Preoxidation on Wear



a. Normalized wear rate



b. Friction coefficient

Figure G-1. Effect of oil degradation on C-93200 bronze contact

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Department of Defense

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| WASHINGTON DC 20310-0500 | | SFAE ASM BV | 1 |
| | | SFAE ASM CV | 1 |
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| FT BELVOIR VA 22060-5843 | | ARMY RSCH LAB | |
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| | | ADELPHIA MD 20783-1145 | |

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| CDR AVIA APPL TECH DIR | | ATCL MS | 1 |
| ATTN: AMSAT R TP (H MORROW) | 1 | FT LEE VA 23801-6000 | |
| FT EUSTIS VA 23604-5577 | | CDR ARMY FIELD ARTY SCH | |
| CDR ARMY ARDEC | | ATTN: ATSF CD | 1 |
| ATTN: SMCAR CC | 1 | FT SILL OK 73503 | |
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| WATERVLIET NY 12189 | | ATTN: ATSE CD | 1 |
| CDR APC | | FT LEONARD WOOD | |
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| NEW CUMBERLAND PA 17070-5007 | | YUMA AZ 85365-9130 | |

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WASHINGTON DC 20375-5342

1

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NAVAL SEA SYSTEMS CMD
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2531 JEFFERSON DAVIS HWY
ARLINGTON VA 22242-5160

1

CDR
NAVAL AIR WARFARE CTR
ATTN: CODE PE33 AJD
P O BOX 7176
TRENTON NJ 08628-0176

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CDR
NAVAL SURFACE WARFARE CTR
ATTN: CODE 63
CODE 632
CODE 859
3A LEGGETT CIRCLE
ANNAPOLIS MD 21402-5067

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1

1

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NAVAL AIR SYSTEMS CMD
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MARINE CORPS SYS CMD
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QUANTICO VA 22134-5080

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PROG MGR COMBAT SER SPT
MARINE CORPS SYS CMD
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QUANTICO VA 22134-5080

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QUANTICO VA 22134-5010

1

PROG MGR GROUND WEAPONS
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2033 BARNETT AVE
QUANTICO VA 22134-5080

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1014 BILLY MITCHELL BLVD STE 1
KELLY AFB TX 78241-5603

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Other Federal Agencies

NASA
LEWIS RESEARCH CENTER
CLEVELAND OH 44135

1

DOE
CE 151 (MR RUSSELL)
1000 INDEPENDENCE AVE SW
WASHINGTON DC 20585

1

DOT
FAA
AWS 110
800 INDEPENDENCE AVE SW
WASHINGTON DC 20590

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